



Calhoun: The NPS Institutional Archive
DSpace Repository

Theses and Dissertations

1. Thesis and Dissertation Collection, all items

1976-06

Improvement of an oil-water pollution monitoring system

Gongaware, William Ralph

Monterey, California; Naval Postgraduate School

<http://hdl.handle.net/10945/17812>

This publication is a work of the U.S. Government as defined in Title 17, United States Code, Section 101. Copyright protection is not available for this work in the United States.

Downloaded from NPS Archive: Calhoun



Calhoun is the Naval Postgraduate School's public access digital repository for research materials and institutional publications created by the NPS community. Calhoun is named for Professor of Mathematics Guy K. Calhoun, NPS's first appointed -- and published -- scholarly author.

Dudley Knox Library / Naval Postgraduate School
411 Dyer Road / 1 University Circle
Monterey, California USA 93943

<http://www.nps.edu/library>

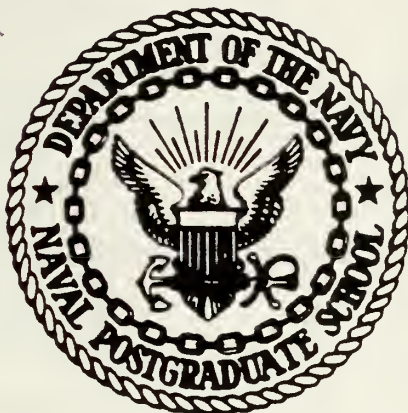
**IMPROVEMENT OF AN OIL-WATER
POLLUTION MONITORING SYSTEM**

William Ralph Gongaware

DANIEL KNOX LOR
NAVAL POSTGRADUATE
MONTEREY, CALIFORNIA

NAVAL POSTGRADUATE SCHOOL

Monterey, California



THESIS

IMPROVEMENT OF AN OIL-WATER
POLLUTION MONITORING SYSTEM

by

William Ralph Gongaware

June 1976

Thesis Advisor:

T. M. Houlihan

Approved for public release; distribution unlimited.

U173530

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

DD FORM 1 JAN 73 1473
(Page 1)

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE(When Data Entered)

The object of the research was to determine operational standards for the type of fluids expected to transport oil into the monitoring system.

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE(When Data Entered)

Improvement of an Oil-Water
Pollution Monitoring System

by

William Ralph Gongaware
Lieutenant, United States Navy
B.S.E.E., North Carolina State University
at Raleigh, 1967

Submitted in partial fulfillment of the
requirements for the degree of

MASTER OF SCIENCE IN MECHANICAL ENGINEERING

from the

NAVAL POSTGRADUATE SCHOOL
June 1976

Thesis
G-5472
c. 1

ABSTRACT

A prototype of an automatic oil monitoring system was improved and used as a tool of research. The system utilizes a direct difference method of total organic carbon determination. The improvements permit a rapid evaluation of the organic carbon content of samples injected into the system to be performed.

The object of the research was to determine operational standards for the type of fluids expected to transport oil into the monitoring system.

TABLE OF CONTENTS

I.	INTRODUCTION-	- - - - -	-11
II.	NATURE OF THE PROBLEM	- - - - -	-19
III.	IMPROVEMENTS CONSIDERED	- - - - -	-21
	A. SAMPLE DELIVERY SYSTEM-	- - - - -	-21
	B. SAMPLE PROCESSING SYSTEM-	- - - - -	-29
	C. COMBUSTION TUBE REPLACEMENT	- - - - -	-33
IV.	OPERATIONAL STANDARD CONSIDERATIONS	- - - - -	-38
V.	COMPARISON CONSIDERATIONS	- - - - -	-40
VI.	IMPROVEMENT SUCCESS CRITERIA-	- - - - -	-42
VII.	PROCEDURES FOLLOWED	- - - - -	-44
VIII.	RESULTS AND DATA-	- - - - -	-46
IX.	CONCLUSIONS	- - - - -	-56
X.	FUTURE IMPROVEMENTS AND RECOMMENDATIONS	- - - - -	-61
APPENDIX A	PARALLEL SYSTEM OPERATION AND CALIBRATION	- - - - -	-69
APPENDIX B	EQUIPMENT OPERATING PARAMETERS-	- - - - -	-72
APPENDIX C	PREPARATION OF SYNTHETIC SEAWATER	- - - - -	-74
APPENDIX D	SAMPLE AGING CONSIDERATIONS	- - - - -	-76
APPENDIX E	CALIBRATION CURVES, CALIBRATION CURVE DATA, TEST RESULTS, AND TEST RESULT DATA-	- - - - -	-77
LIST OF REFERENCES	- - - - -	- - - - -	-97
INITIAL DISTRIBUTION LIST-	- - - - -	- - - - -	-98

LIST OF TABLES

Table		Page
I	Equipment Operating Parameters as of Fiscal Year 1975 - - - - -	12
II	NSRDC Annapolis Samples Processed by CCl ₄ - I. R. Spectrometer Method- - - - -	41
III	3 February 1976 Calibration Curve Data - - - - -	82
IV	4 April 1976 Calibration Curve Data- - - - -	83
V	7 April 1976 Calibration Curve Data- - - - -	84
VI	23 April 1976 Calibration and Comparison Curve Data - - - - -	85
VII	Oil Concentration Calibration Curve Data - - - - -	87
VIII	Synthetic Seawater Results - - - - -	88
IX	Synthetic Sea Water Data - - - - -	89
X	Natural Seawater Results - - - - -	91
XI	Natural Seawater Data- - - - -	92
XII	Comparison between Parallel System and CCl ₄ I. R. Spectrometer Method - - - - -	94
XIII	Bilge Water Test Results - - - - -	95

LIST OF FIGURES

Figure		Page
1	Sample Peak Heights- - - - -	14
2	Initial System Schematic - - - - -	16
3	Sample Manifold- - - - -	23
4	Sample Delivery System Mounted on Side of Sample Injector- - - - -	24
5	Masterflex Tubing Head - - - - -	25
6	Masterflex Tubing Pump Power Control Circuit- - - - -	27
7	Masterflex Tubing Pump Power Control Circuit Components - - - - -	28
8	Condenser Connections- - - - -	30
9	Parallel System Schematic- - - - -	32
10	Total Carbon Combustion Tube Replacement - - - -	35
11	Total Carbon Combustion Tubes- - - - -	37
12	Pump Speed Test Results- - - - -	47
13	2 February 1976 Calibration Curve- - - - -	77
14	4 April 1976 Calibration Curve - - - - -	78
15	7 April 1976 Calibration Curve - - - - -	79
16	23 April 1976 Calibration and Comparison Curve - - - - -	80
17	29 April 1976 Oil Calibration Curve- - - - -	81
18	Monel Total Carbon Combustion Tube after Failure- - - - -	51
19	Monitoring System Modified to Operate as a Parallel System - - - - -	54

Figure		Page
20	Parallel System Sample Peak Total Organic Carbon Heights - - - - -	55
21	Sample Delivery System Improvement Possibility- - - - -	62
22	Sliding Block Valve Improvement Possibility- - - - -	64
23	Rapid Pulse System Expected Output- - - - -	66
24	Fast Acting Sample Supply Manifold - - - - -	67

TABLE OF ABBREVIATIONS

<u>Abbreviation</u>	<u>Definition</u>
IC	Inorganic Carbon
OC	Organic Carbon
TIC	Total Inorganic Carbon
TOC	Total Organic Carbon
TC	Total Carbon
PPM	Parts per million
NDIRA	Non-Dispersive Infrared Analyzer
CCl ₄	Carbon Tetrachloride
CO ₂	Carbon Dioxide
EPA	Environmental Protection Agency
TEP	Temperature Extreme Pressure
NDFO	Naval Distillate Fuel Oil
IR	Infrared
NSRDL	Naval Ship Research and Development Laboratory
ER	Engine Room
FR	Fire Room
BSC	Beyond the Scope of the Calibration Curve
NPS	Naval Postgraduate School

ACKNOWLEDGEMENT

The author wishes to express his sincere thanks to Dr. Tom Houlihan for allowing him to turn his ideas into operating components of a pollution monitoring system.

A note of thanks to Tom Christian, Roy Edwards, Ken Grahlan, and Ms. Vicki Culley who with their knowledge and expertise in their respective fields were of immense aid in this research. Lastly, to my wife, for her help and understanding, my appreciation is forwarded with fondest regards.

I. INTRODUCTION

In FY 75 the prototype of an automatic oil pollution monitor was built and tested as described in Ref. 1. In the system developed, a direct difference method of total organic carbon determination was utilized to ascertain oil concentrations. Using this monitor, it was possible to specify the concentration of any oil, independent of type, in a known water sample. In the final phase of the study, preliminary investigations on prototype improvements and oil concentrations in bilge water were initiated.

The system operating parameters are given in Table I.

The monitoring system described in Ref. 1 was capable of processing a sample every four minutes and delivered a recorded output in the form of peak heights as shown in Figure 1. The smaller peak heights were proportional to the inorganic carbon (IC) content of the sample and the higher peak heights were proportional to the total carbon (TC) content of the sample. These peak heights were compensated to account for (1) the different sample sizes injected into the combustion tubes of the unit, and (2) the different fluids used to transport a sample into these combustion tubes. The compensated peak heights were then converted to ppm of carbon using appropriate calibration curves. Finally, the total organic carbon (TOC) in ppm was

TABLE I EQUIPMENT OPERATING PARAMETERS AS
OF FISCAL YEAR 1975

I. Beckman Model 915 Sample-Inject Furnace Module

A. Total Carbon Channel Specifications

1. Carrier gas.....CO₂ free air
2. Flow rate.....250 cc/min
3. Pressure.....4 psi
4. Combustion tube.....ceramic
5. Catalyst.....Cobalt oxide
6. Temperature.....950°C

B. Inorganic Carbon Channel Specifications

1. Carrier gas.....CO₂ free air
2. Flow rate.....250 cc/min
3. Pressure.....4 psi
4. Combustion tube.....Vycor glass
5. Catalyst.....85% Phosphoric Acid-
Soaked Quartz chips
6. Temperature.....150°C

II. Non-dispersive Infrared Analyzer Beckman

Model 865 at a gain of 700

III. Hewlett-Packard Potentiometric 10-in. recorder

set for 0.5 in/min

A. Channel 1-10.0 mv range

B. Channel 2-100.0 mv range

TABLE I (continued)

- IV. Ionics Sliding Block valves at a 35 psi
switching pressure
 - A. IC channel.....20 ml sample size
 - B. TC channel.....40 ml sample size
- V. Masterflex tubing pump-setting of 5

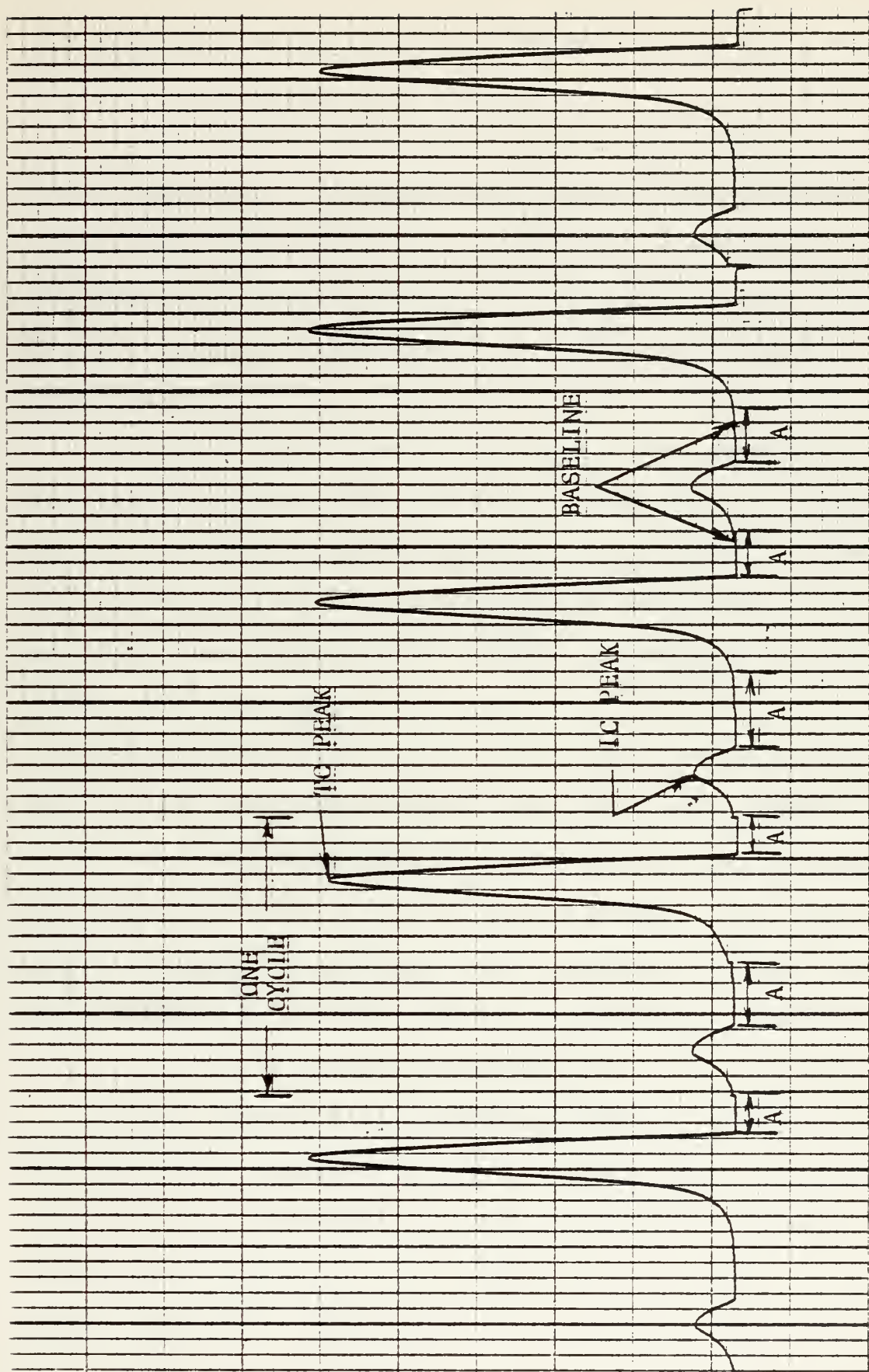


FIGURE 1. SAMPLE PEAK HEIGHTS

determined by subtracting the inorganic carbon (IC) values from the total carbon (TC) values.

The monitoring system could detect the concentration of any type of oil in water utilizing but one calibration curve. The particular oil standard curve that related the recorded peak heights to the oil concentration was found to be a constant (1.17) times the carbon concentration curve values.

The system functioned in the following manner when operating as prescribed in Table I. Referring to Figure 2, the water sample is pumped continuously through the two rulon sliding block valves and samples are taken at a specified time interval the duration of which is controlled by two rotating cams.

When a TC reading is to be taken the sample is swept into the TC (high temperature) combustion tube immediately after the second sliding block valve where it is oxidized and vaporized into CO₂ laden gas and steam. The vapor then passes through the stainless steel condensers where the vapor condenses into water and is collected in the oversized piping serving as a reservoir.

The CO₂ laden gas is directed through a filter to the Non-Dispersive Infrared Analyzer (NDIRA), which is sensitized to CO₂. The NDIRA produces an electrical signal output which registers on a strip chart recorder as a peak which is directly proportional to the total amount of carbon (TC) in the injected sample.

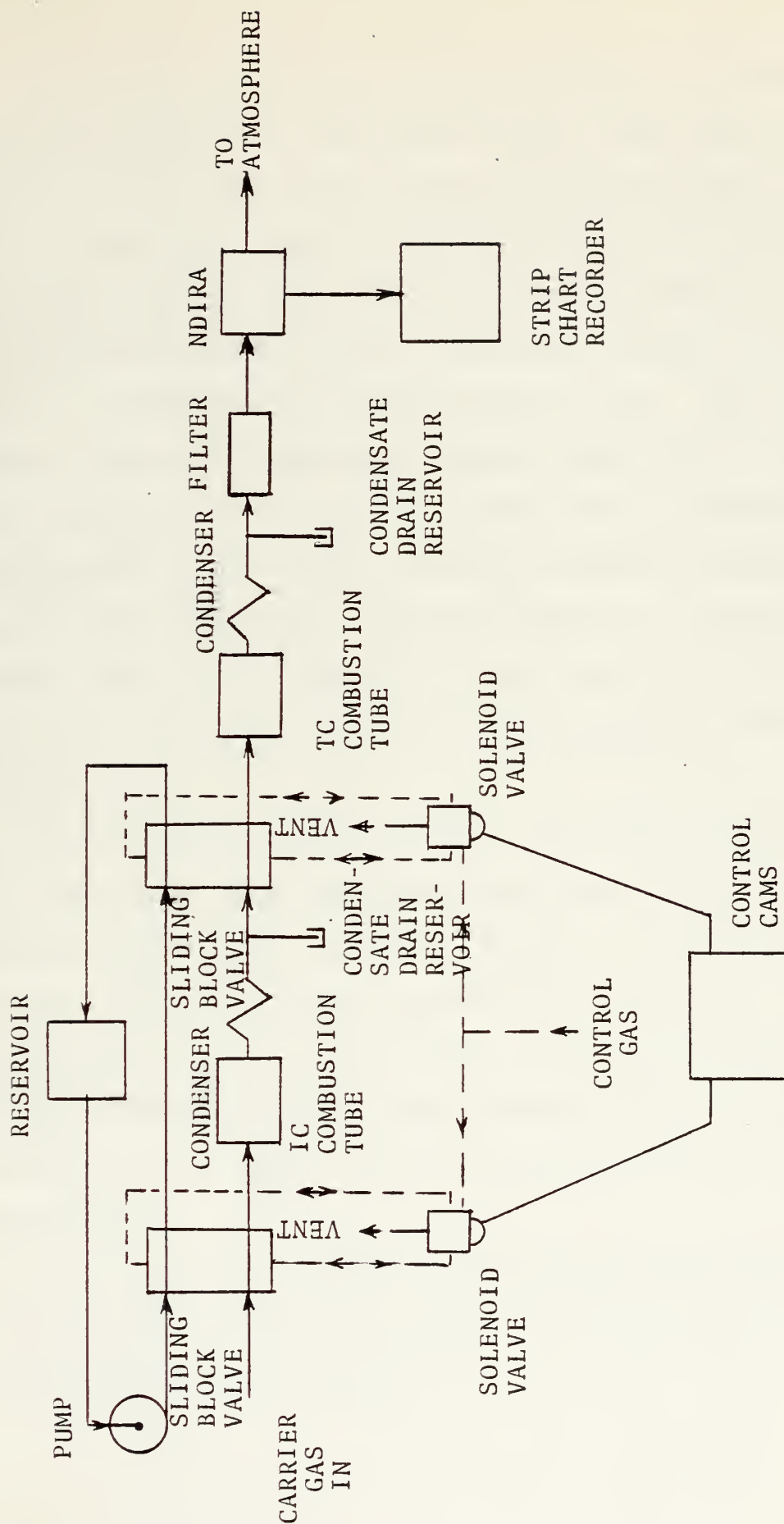


FIGURE 2. INITIAL SYSTEM SCHEMATIC

The processing of the IC sample involves a passage first through the IC (low temperature) combustion chamber located immediately after the first sliding block valve. The CO₂ laden gas output of the IC condenser is fed via the total carbon rulon valve into the TC combustion chamber (to minimize baseline drift), and then through a filter into the NDIRA analyzer (sensitized to CO₂). Now the NDIRA produces an electrical signal output which registers on a strip chart recorder as a peak which is directly proportional to the total amount of inorganic carbon (TIC) in the injected sample. The total amount of organic carbon (TOC) in the sample is simply the difference between the total carbon (TC) and the total inorganic carbon (TIC) values.

The operation of the sliding block valves is controlled by timing cams which determine when the sliding block valves change their position. Control of the sliding block valves is important because the valves must inject the samples at the proper moment, remain stationary to avoid interfering with a sample being processed, and reposition at the proper time to accomplish the previous two requirements.

In order to obtain meaningful results from the system several samples had to be processed and average values determined from the results.

The following specifications were given as the optimum parameters for a monitoring system and were used as goals during the building and testing of the present unit:

1. be reliable and rugged enough to be used in a shipboard environment.
2. have a response to a particle size of 50 microns.
3. operate in a temperature range of 40°F to 120°F.
4. have a fast response time.
5. be independent of oil type.
6. have an accuracy of ± 0.5 ppm in a 0 to 50 ppm range.
7. have a digital read-out in ppm.
8. have automatic ranging.
9. be self-calibrating and ranging.
10. be self-purging and cleaning.
11. have short warm-up and stabilization times.

II. NATURE OF THE PROBLEM

The object of the work done during this period on the system described in the introduction was:

1. To modify the system to reduce the amount of time between the moment a sample is injected into the combustion tubes and the moment a peak height which is proportional to the total organic carbon content is recorded on the strip chart recorder;
2. To obtain an operational standard for the carbon content of seawater by comparing natural seawater to a synthetic seawater;
3. To compare the results of samples processed by the system developed to the results of samples processed by the CCl_4 -I.R. Spectrometer method.

To achieve these general objectives several improvements were necessary. The scope of these alterations are discussed in the next paragraphs.

The first improvement affected the sample delivery system. The modification was necessary to change the system to a one-pass system in which only a small sample had to be treated. If the original sample delivery system were to be used as a continuous one-pass system, it would have required approximately 1100 milliliters per four-minute

sample. In addition to this volume, an amount of sample required to fill the delivery tubing, to purge the tubing of the previous sample, and to remove any air bubbles which are trapped in the tubing would have had to be used.

The next two modifications altered the carrier gas delivery system to reduce the amount of system turn-around time. As these modifications were being designed and constructed considerations were given to improving the system's ruggedness for operation in a shipboard environment.

Referring to Figure 1, the part of the strip chart output labeled with an A was considered to be dead time during which the system was sitting idle. The first improvement removed approximately 80 seconds of this dead time. The second improvement reduced the turn-around time from the original four minutes to about 90 seconds. Ultimately, turn-around times in the neighborhood of 60 seconds were achieved.

III. IMPROVEMENTS CONSIDERED

This section contains the design considerations used to improve the monitoring system.

A. SAMPLE DELIVERY SYSTEM

To reduce the amount of sample required the avenues open were:

1. reduction of the speed of the system pump,
2. mounting the pump in close proximity to the first rulon sliding block valve,
3. construction of the system so that it is self-priming and self-purging of previous samples and air bubbles,
4. construction of a manifold that will allow samples to be selected for processing as they are needed.

In order to make the system self-purging the components were assembled in such a manner that the first rulon sliding block valve inlet was at the highest point in the system. Each component between the sliding block valve inlet and the sample container was located successively lower than the previous component.

The manifold was constructed to allow a choice of three samples. It was fabricated from plexiglass to allow observation of the samples as they passed through the manifold to determine if any build-up of foreign matter or sample separation occurred. The ports of the manifold were

arranged so that the outlet port is at the top, the sample inlet port is below the outlet port, the cleaning agent inlet port is below the sample inlet port, and the purging agent inlet port is the lowest inlet port. This configuration was necessary to achieve an efficient cleaning of the manifold and tubing and to allow the purging agent to purge all the material previously pumped through the manifold. Reference 2 was used to confirm that plexiglass had a low water absorption characteristic and was hardly affected by the samples expected to pass through it.

The manifold is shown in Figure 3. Valve A was used to admit distilled water which was used as a purging agent. Valve B controlled the sample being processed. Valve C had the dual function of either being used as a drain or as a source of another sample.

Connection D is the manifold outlet to the intake of the pump which was mounted directly above the manifold. The pump and manifold were mounted on the side of the Beckman 915 Carbon Analyzer in the proximity of the first rulon valve as shown in Figure 4.

The masterflex tubing pump was modified several ways to improve its performance in the system. First, the flexible tubing path through the tubing pump head was rerouted as shown in Figure 5. Herein, the left picture shows the original tubing route and the right picture shows the modified tubing route. The modification allowed

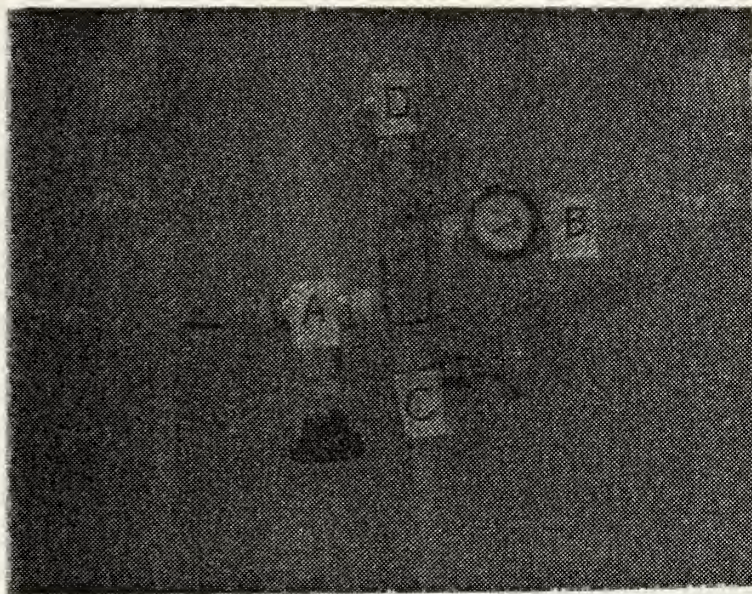


FIGURE 3. SAMPLE MANIFOLD

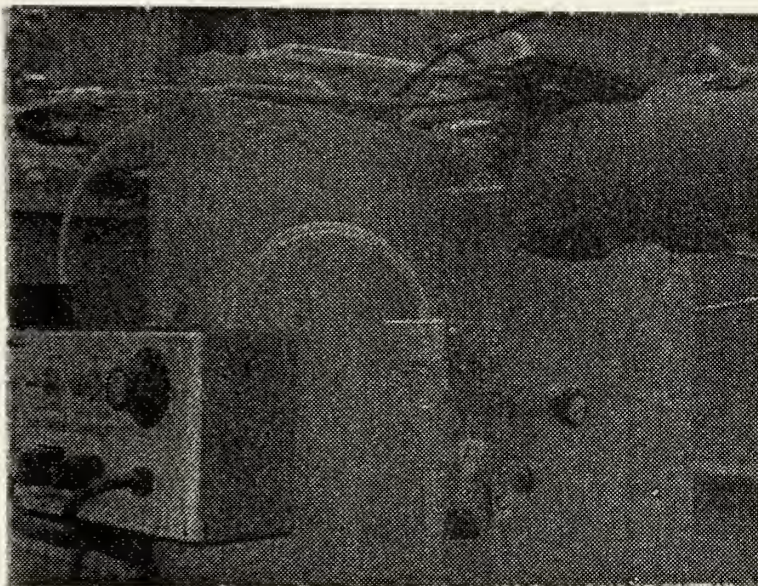


FIGURE 4. SAMPLE DELIVERY SYSTEM MOUNTED ON
SIDE OF SAMPLE INJECTOR

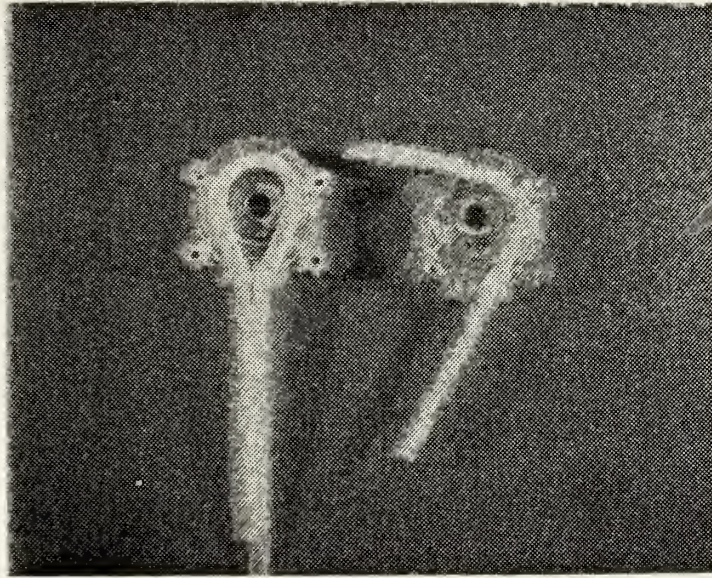


FIGURE 5. MASTERFLEX TUBING PUMP HEAD

Left side - before modification.

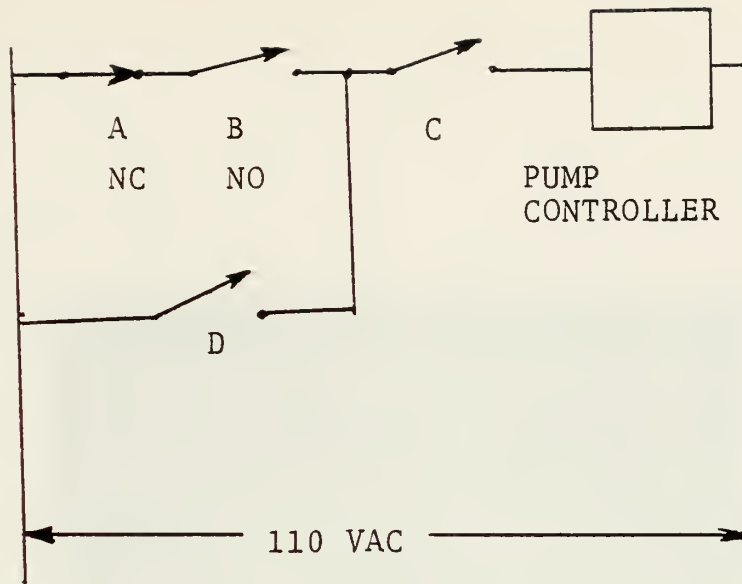
Right side - after modification.

any trapped bubbles of air to rise to the highest point in the tubing circuit, namely the sliding block valve.

The second possible modification to the pump concerned the controller. The power to the controller could be turned off and on using the circuit of Figure 6. Switches A and B were controlled by cams driven by the same motor which controlled the sliding block valves. Switch A was opened whenever the pump was not running and switch B was closed when the pump was running. Switch D was used to override the cam control switches. Switch C provided for positive control over the pump without rotating the speed control knob to the off position. This was necessary because the speed control knob graduations were for reference only and were not calibrated.

The cams controlling the switches in the pump power circuit allowed the pump sufficient time to attain its operating speed before any sample was extracted and continued pumping until the last sample was extracted. The cam for switch B was cut with two arcs of ten degrees located 180° to each other and then shortened as necessary to minimize the sample size. The cam for switch A was cut with an arc of approximately 30° . Figure 7 shows the pump power control circuit components.

It must be noted here that the present system depends upon a homogeneous sample as explained in Ref. 1. Using the cam controlled pump allowed the sample to sit stagnant



NC = NORMALLY CLOSED

NO = NORMALLY OPEN

FIGURE 6. MASTERFLEX TUBING PUMP
POWER CONTROL CIRCUIT

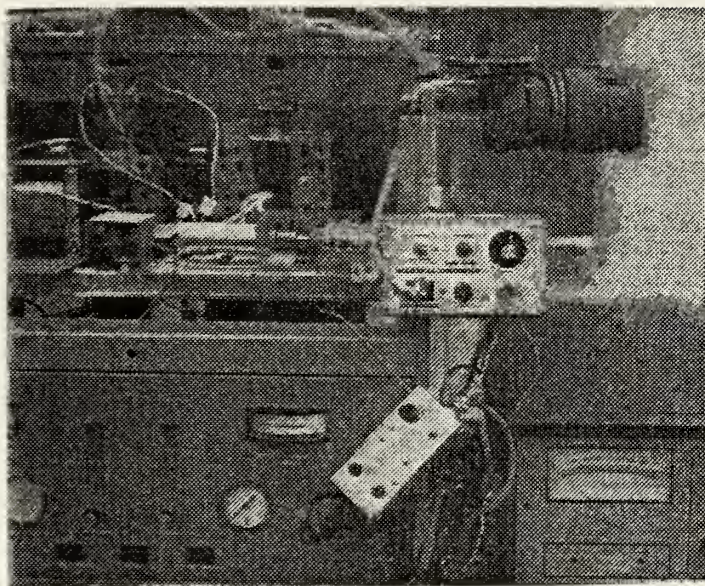


FIGURE 7. MASTERFLEX TUBING PUMP POWER
CONTROL CIRCUIT COMPONENTS

in the tubing between sample extractions. Closing switches D and C overcame this situation because it returned the sample delivery system to a continuous-flow system.

B. SAMPLE PROCESSING SYSTEM

To reduce the turn-around time for the system, two approaches were considered. The first was the removal of all unnecessary tubing between the sample select sliding block valve and the NDIRA. This was accomplished in two ways:

1. by locating the NDIRA as close as possible to the condenser outlet, and
2. by attaching the condenser inlet directly to the outlet of the combustion tubes.

The attachment of condensers to the combustion tube was achieved by using a stainless steel swagelok bulkhead union. First, one end of the swagelock fitting was drilled out to accommodate the condenser piping end and then it was silver-soldered to the condenser piping. The modified condenser was attached to the fitting at the outlet of the combustion tube using a short piece of stainless steel tubing and swagelock fittings. The condensers were mounted with a downward slope to facilitate condensate drainage. The condenser outlet was placed in a vertical position to reduce the possibility of condensate being carried downstream into the system components. These modifications are shown in Figure 8.

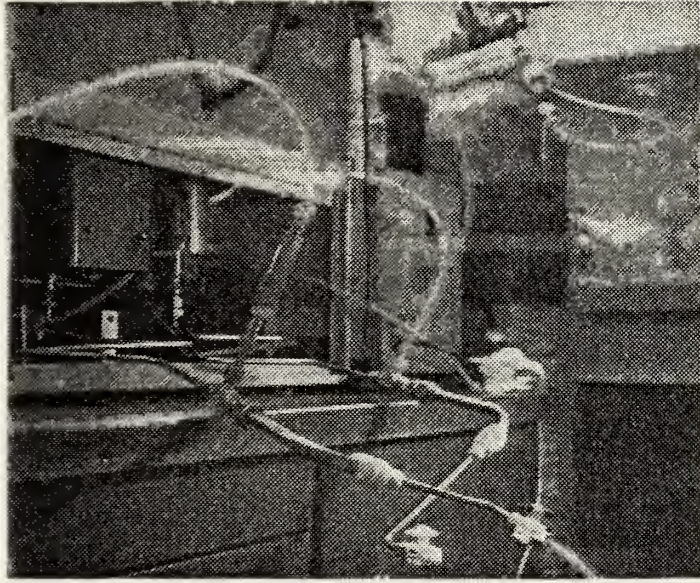


FIGURE 8. CONDENSER CONNECTIONS

The second approach taken to reduce the turn-around time is shown in Figure 9. This improvement consisted of changing the sample processing system from a tandem system to a parallel system which processes the total carbon sample at the same time the inorganic sample was being processed. The readings from the two NDIRA analyzers were processed as shown using analog modules to compensate and to subtract the two NDIRA readings to give organic carbon content directly in the form of a peak height on a strip chart recorder.

Input B was developed using the D.C. power supply which drove the cam motor. The purpose of input B was to supply a baseline constant which could be subtracted as necessary. For example, this constant could be used when working with distilled water samples to subtract the distilled water total carbon content from the total carbon content of the sample.

The calibration and operation of the system arranged in this manner is described in Appendix A. Initially the operating parameters listed in Table I were used for the parallel system operation and calibration.

In order to achieve a meaningful peak height output of organic carbon content, the two NDIRA analyzers must produce their maximum outputs simultaneously. Because the data processing system is presently a slow reacting analog system, the assumption was made that the electronic components

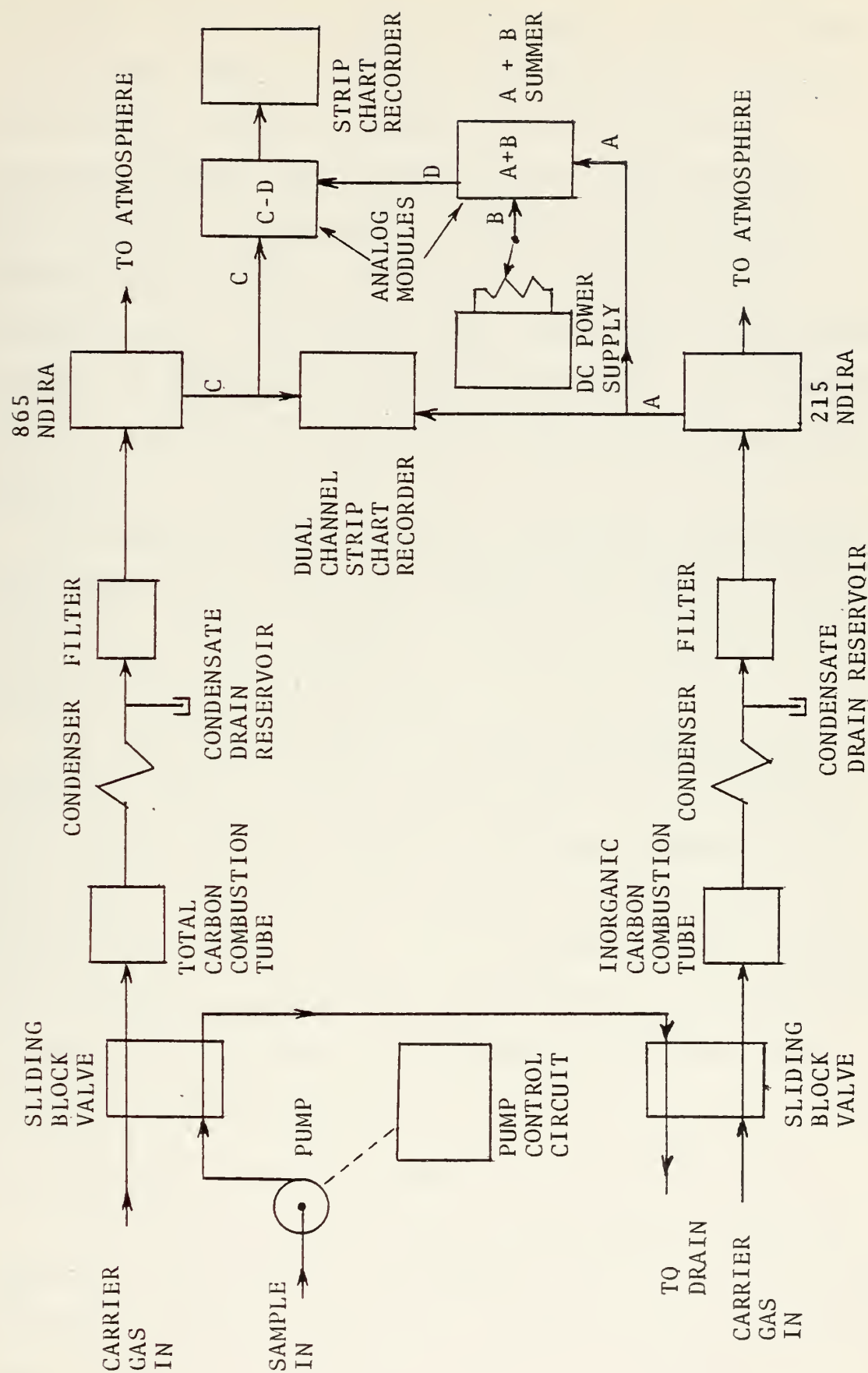


FIGURE 9. PARALLEL SYSTEM SCHEMATIC

installed in the system would not produce any significant delay times. There were three ways available to control the system's response in order to have the IC and TC processes produce their maximum outputs simultaneously. The first was to control the time when the samples are selected by the sliding block valves. This could be accomplished by rotating the cams which control the solenoid valves that operate the sliding block valves. Initially the valves were operated simultaneously and adjustments made as necessary.

The second method of control consisted of varying the flow rate of the carrier gas through the system. The third method of control considered variation of the pressure of the carrier gas in the system.

The cam which controlled switch B of Figure 6 was aligned to operate switch B during the time the samples were being extracted. Then the cam which operated switch A of Figure 6 was aligned to operate switch A before the switch B cam rotated 180°. This arrangement kept the pump from operating unnecessarily and permitted a reversion back to the original tandem pass configuration if conditions warranted such a procedure.

C. COMBUSTION TUBE REPLACEMENT

A tube used to replace any of the presently installed combustion tubes had to successfully duplicate the functions performed by the original tube. A few of these requirements were:



1. operate at the correct temperature,
2. fit inside the present furnace,
3. support the catalyst,
4. permit proper carrier gas flow rates,
5. adapt to the components presently installed in the system,
6. remain inert to its environment, catalyst, gases, or samples to which it is exposed.

Using Refs. 4 and 5, Monel was selected as the material from which to manufacture the replacement tubes.

The 17-5/8-inch-long inorganic combustion tube replacement was made from a piece of Monel tubing with an ID of 1/2 inch and 5/8 inch OD. A catalyst support in the form of two 0.040-inch nichrome wires crossed perpendicular to each other was located 9-1/4 inches below the top of the tube. These nichrome wires were silver soldered in place. The Monel tube was adapted to the rulon sliding block adapter using a machined teflon insert to extend and to align the tube. At the bottom of the tube a Monel plug was inserted and tapped with 1/8-inch pipe threads into which a swagelok adapter was threaded.

The Total Carbon Combustion tube constructed as shown in Figure 10 was manufactured from two pieces of Monel. The two pieces were then tapped and threaded with pipe thread in order to obtain a tight fit. The taper at the top was necessary to adapt the replacement tube to the existing rulon sliding block adapter. The connection at



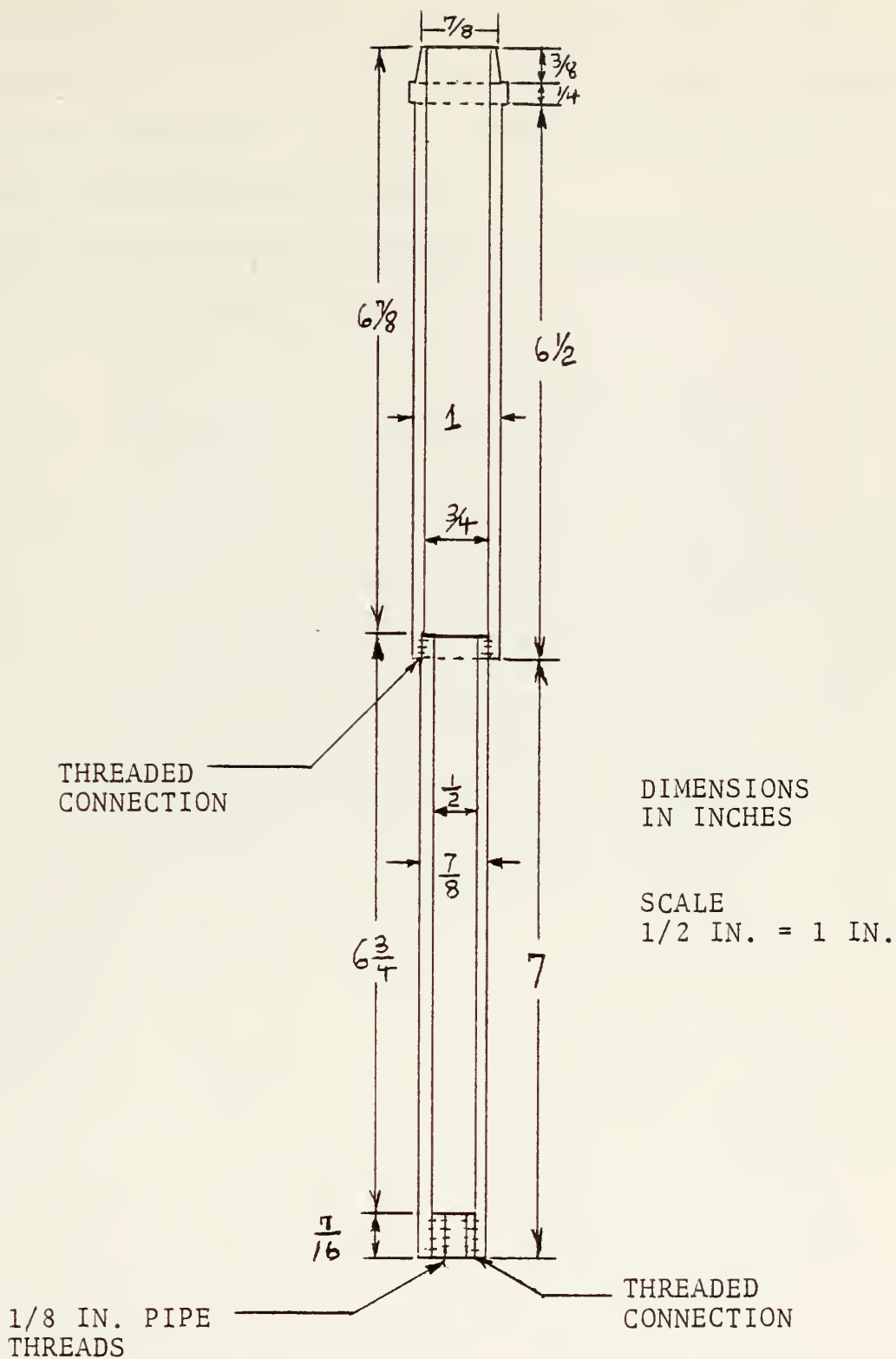


FIGURE 10. TOTAL CARBON COMBUSTION
TUBE REPLACEMENT



the bottom of the tube was made with a Monel plug which was tapped with 1/8-inch pipe threads into which a swagelok adapter was threaded. Figure 11 shows the TC tubes in the furnaces for comparison purposes.

The flow rate of both replacement combustion tubes was tested as recommended in Ref. 8.

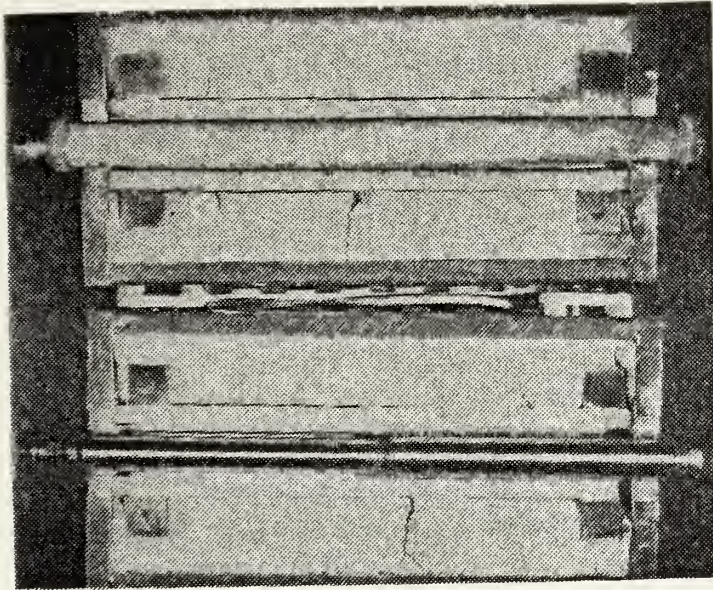


FIGURE 11. TC COMBUSTION TUBES

Upper - Ceramic

Lower - Monel replacement

IV. OPERATIONAL STANDARD CONSIDERATIONS

The ultimate goal of the monitoring system being improved during this period was to determine how much organic carbon is added to initially oil-free water when oil and water are mixed together on board U. S. Navy ships. The purpose of an operational standard was to establish the contents of the initially oil-free water so that it can be subtracted from results obtained when processing contaminated samples. Thus, knowing the operational standard for a particular processing method and water base, a rapid determination of oil contamination to water on board ships could be achieved.

For this particular monitoring system standard values can be subtracted from the output system by being used as bias inputs at port B of Figure 9.

Reference 6 reported that seawater is part of the water which makes up bilge water. Reference 8 reports that there exists a synthetic seawater endorsed by the Environmental Protection Agency (EPA). The fabrication of this synthetic seawater is described in Appendix B.

An operational standard for synthetic seawater was established by processing approximately 50 samples of synthetic seawater to obtain its average organic carbon content. Then the same number of natural seawater samples were processed with the system to also determine the

organic carbon content of natural seawater. The two results were then to be compared.

V. COMPARISON CONSIDERATIONS

In order for a new system to be accepted as a valid substitution for existing systems, it must be able to duplicate results previously produced by the machine it intends to displace. In this study, such a comparison was accomplished using pollution samples from two sources. The first source of samples was NSRDC, Annapolis. The samples listed in Table II were randomly selected from a batch of samples that had been processed at Annapolis. The concentrations given are the results obtained when the sample batch had been processed using the CC14 I. R. Spectrometer method.

The second source of samples was bilge water removed from operational Navy ships. The samples were collected as prescribed in Ref. 6 in order to duplicate the results displayed therein for the three layers of bilge water.

All the samples processed by this system were prepared and handled as outlined in Ref. 1.

SAMPLE NUMBER	CONCENTRATION RANGE IN PPM
NDFO	
2	5 - 7
12	18 - 20
22	32 - 35
32	55 - 64
2190 TEP	
2A	4
12A	DESTROYED IN SHIPPING
22A	45 - 60
32A	52 - 68

TABLE II NSRDC ANNAPOLIS SAMPLES
 PROCESSED BY CCl_4 - I. R.
 SPECTROMETER METHOD

VI. IMPROVEMENT SUCCESS CRITERIA

The tandem system described in the introduction was a linear system that was capable of specifying the concentration of oil in water. The system depended upon a linear calibration curve relating carbon concentration to ppm of oil. Reference 1 established that a carbon standard calibration curve can be related to the oil standard calibration curve by a constant.

Any system improvements were considered successful if after the improvement was installed and operated for a reasonable amount of time a linear calibration curve was obtained using standards prepared in accordance with Ref. 1.

When the parallel system became operational a constant relating the oil standard calibration curve to the carbon calibration curve was determined. Even though a single linear calibration curve would establish the capability of the parallel system, a series of calibration curves comparing the two methods were made to determine if any capability was lost due to alterations.

The calibration curves were drawn using the average results from a minimum of four samples. These four peak heights were obtained after the system had established a constant baseline and the peak heights consistently

repeated around a value which indicated that the system had purged itself of previous processed samples.

VII. PROCEDURES FOLLOWED

The previous sections described the improvements that were considered and the research conducted using this particular TOC monitoring system. The procedure followed in each endeavor is outlined in the following three steps:

1. An improvement was installed and made operational.
2. A calibration curve or other plot was obtained to determine if the improvement was successful.
3. Several samples were processed to obtain data.

If step 2 was not successful, steps 1 and 2 were repeated as necessary until the desired success was obtained. Once step 3 was completed the next improvement was attempted. This procedure was considered necessary because if all the improvements had been installed initially and some were not successful, considerable amounts of time would have been spent locating the cause of particular problems.

All the planned improvements and research were completed, with two exceptions, by the above procedure.

The first exception concerned the pump speed setting. This setting was determined by operating the system and gradually reducing the pump speed until erratic results appeared. The fluid used for this determination was tap water. Tap water was chosen because it is available in large quantities, the only requirement being that sufficient quantity for the entire test had to be collected before the start of the test.

The monitoring system was set to process a minimum of eight samples for each pump speed setting selected. These results were averaged to determine which pump speed could be used to supply samples and still provide useable results.

The second exception occurred when the tandem system was changed to a parallel system. Because the monitoring system output depended upon the condition of the catalyst in the combustion tubes, the calibration curves comparing the tandem system to the parallel system had to be obtained in a close time frame. In order to achieve this, these two curves were obtained by switching the system alternately between the parallel mode of operation and the tandem mode of operation for each standard processed.

VIII. RESULTS AND DATA

All the improvements were successfully installed and operated except for the total carbon combustion tube replacement attempt. Figure 12 displays the Masterflex Tubing pump results. Erratic peak heights were obtained when operating below a pump speed setting of 2. The pump was operated at a setting of 3 for all tests conducted during this time period.

The improvements installed and the conversion to a parallel system resulted in an average turn-around time of 55 seconds. Along with this time reduction the flow rate and operating pressures were reduced to 160 cubic centimeters per minute and three psi respectively.

The 55-second turn-around time allowed the NDIRA just enough time to return to the baseline before it had to respond to the next sample being processed. No noticeable temperature drop occurred in either combustion tube furnace while operating as a parallel system. Valves were installed on the condensate reservoirs to facilitate easier drainage of the reservoirs.

During the operation of the system, the cycling of the solenoid valves which control the rulon sliding block valves would cause the pens of the strip chart recorders to jump. This would interfere with the recording of the peak heights and baseline values. Thus, when a sample of low carbon

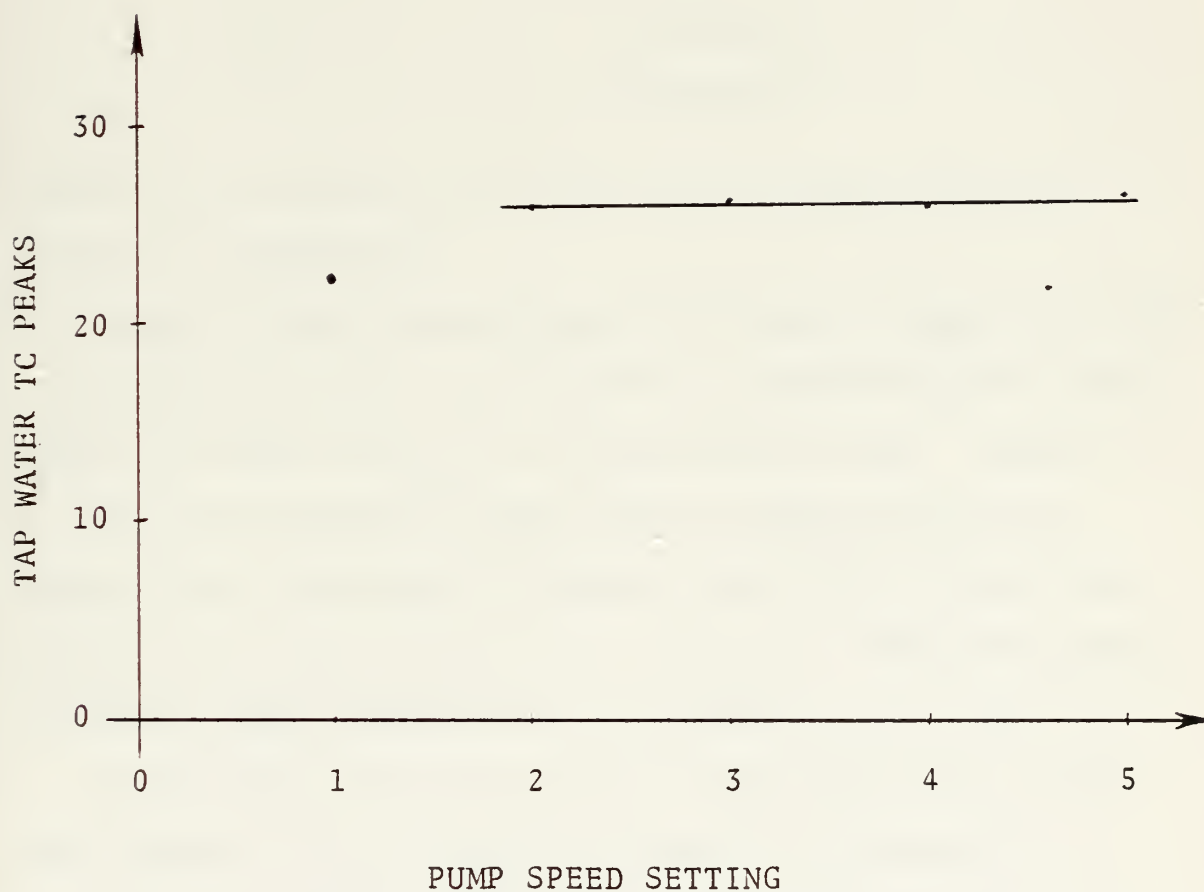


FIGURE 12. PUMP SPEED TEST RESULTS

concentration was processed, the data collected was considered to be approximate and unreliable.

The calibration curves obtained during this period were all linear and are given in the following figures:

Figure	Calibration Curve Data
13	2 Feb 76
14	4 April 76
15	7 April 76
16	23 April 76
17	29 April 76

Figures 13 through 17 and Tables III through XIII are located in Appendix E.

Figure 16 has a dual purpose of being a comparison and a calibration curve, the comparison representing the shift from the tandem system to the parallel system. Figure 17 is the oil calibration curve used in conjunction with Figure 16 to determine if the oil and carbon calibration curves were still related by a constant. Using the method of Ref. 1, this constant was determined to be 1.13.

Tables III, IV, V, VI, and VII give data used to plot the Figures 13 to 17 and are located in Appendix E.

For the synthetic seawater a total of 59 samples were processed on three different dates yielding an average organic carbon content of 24.2 ppm. Table VIII contains the data used for this determination and Table IX contains the data used to calculate Table VIII.

For the natural seawater 56 samples were processed on three different dates yielding an average organic carbon content of 28.9 ppm. Table X contains the data used for this determination and Table XI contains the data used to calculate Table X.

The results from the comparison test for the samples obtained from NRSDC, Annapolis appear in Table XII. The system gave a lower concentration than the range of concentrations provided by NRSDC except for the samples in the low concentration range (see Appendix D). The system had trouble processing the 2190 TEP oil samples which had oil concentrations greater than 50 ppm. The system pressure and flow rate had to be lowered to keep these particular samples in the combustion tube for a longer period of time. No problems were encountered while processing the NDFO samples.

The results from the bilge water test are given in Table XIII. The samples collected from the engine room did not yield useable results because the bilge water was located beneath a layer of oil approximately one-quarter of an inch thick. This gave results beyond the range of the calibration curves and beyond the design parameters for the monitoring system as listed in the introduction. The fire room samples were collected under better conditions. The 11.0 ppm result was obtained without subtracting any constants for feed water.

The total carbon combustion tube replacement as shown in Figures 10 and 11 did not operate successfully. After being heated to 950°C for approximately 23 hours, the interior and exterior surfaces were oxidized. The oxidation rate was high enough to cause large flakes of metal to fall from both surfaces. The oxidation rate was greatest on the exterior surfaces of the tube. The interior surface was exposed only to nitrogen and carbon dioxide free air. Figure 18 shows the effect of the oxidation of the TC combustion tube. The exterior oxidation layer is about twice as thick as the interior oxidation layer.

Another problem that became apparent with the TC combustion tube was the amount of heat transferred to the other components in the system. Before any modifications had been made to the TC combustion tube, the connecting ceramic tube and the Tygon tubing acted as insulators to any heat transfer. When the system was changed to an all-metal system the nearby sliding block rulon valve and stainless steel condenser became extremely hot. The high temperature of the sliding block rulon valve was also maintained by a flue effect established by the replacement TC combustion tube not filling the TC furnace as completely as the ceramic tube as shown in Figure 11. This also contributed to the high oxidation rate sustained by the tubes. The Monel IC combustion tube operated satisfactorily at its 150°C temperature. The Monel tubes (both TC and

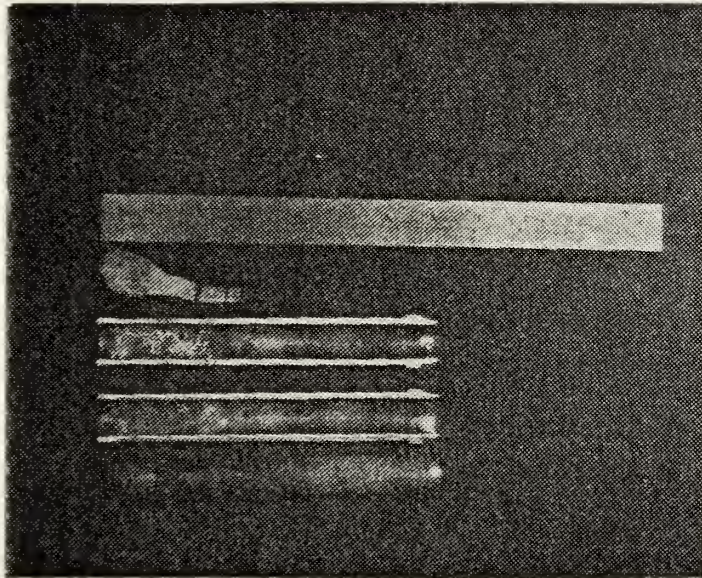


FIGURE 18. MONEL TC COMBUSTION TUBE AFTER
FAILURE, DISASSEMBLED, UPPER
SECTION CUT IN HALF, AND METAL
FLAKES

IC) did not react with the catalysts or samples injected into them.

As the system was improved and the turn-around time was reduced the required sample size was likewise reduced. The sample delivery system as improved operated in an excellent manner. The manifold and tubing were self-purging except when small bubbles became entrapped in the upper corners of the manifold plenum. The manifold was mounted using a hinge to allow it to be tilted as necessary to remove these bubbles. The bubbles could be removed automatically and the manifold remounted on a solid base by tapering the fluid path upward from the manifold plenum to the outlet port. The pump control circuit and manifold were able to be manipulated to allow a change from one sample to another sample (or purging agent) in less than one minute. This period included the time spent in draining the manifold of the previous fluid, pumping the new fluid into the system, and ensuring that entrapped bubbles were removed. The final sample size required was 150 milliliters for an homogeneous sample and approximately 500 milliliters for a continuously pumped sample. These sample sizes allow a minimum of eight to ten samples to be processed including the sample necessary to fill the tubing, to purge any gas bubbles, and to remove the previous sample from the tubing.

Samples that were not homogenized were processed with a blender and ultra-sonic cleaner as described in Ref. 1.

The flow test of Ref. 8 was conducted and for both replacement combustion tubes the pressure drop was less than 0.1 cm of mercury.

The parallel system as operated during this time period is shown in Figure 19. The peak heights recorded as output for the parallel system are shown in Figure 20.

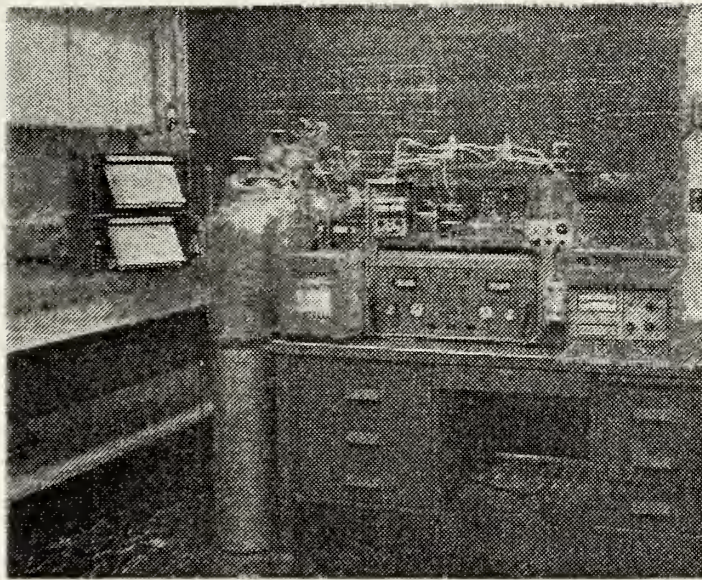
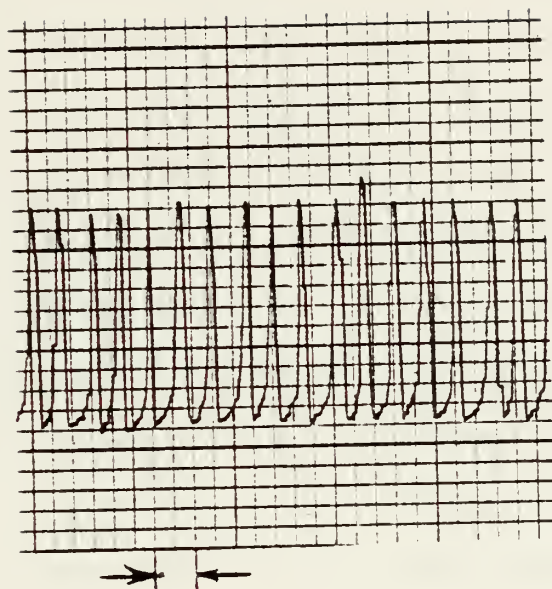


FIGURE 19. MONITORING SYSTEM MODIFIED TO
OPERATE AS A PARALLEL SYSTEM



1 minute

FIGURE 20. PARALLEL SYSTEM SAMPLE
TOC PEAK HEIGHTS

IX. CONCLUSIONS

The monitoring system as improved has proven its ability to process samples of oil in bilge water. The system still has to be maintained as outlined in Ref. 1. The system is not operating at its maximum because two components, the Beckman 915 Sampler and the NDIRAs, are not being driven to their peak potential. The technical manuals for the NDIRAs describe the analyzers as continuous analyzers while they are being used to analyze pulses. The Beckman 915 Sampler-inject/Furnace module does not appear to be operating at its maximum potential because:

1. the temperatures of the ovens remained constant when operating as a parallel system,
2. no condensate was being collected in the IC condensate reservoir,
3. the flow rates of both channels were reduced.

The parallel system saves considerable time when compared to the tandem system. The tandem system requires either two calibration curves or compensation of the data to use one calibration curve. This compensation requires knowing the required calibration constants to obtain useable results. The gains of the analog module amplifiers and the NDIRAs and the input to port B can be altered to insert these constants directly into the output.

The parallel system results when compared to the initial system results show excellent correlation. This

is evidenced by the coincident calibration curves of Figure 16.

A difficulty which was encountered during this study occurred when the system was expected to process samples which contained concentrations of oil greater than the monitoring system specifications listed in the introduction. The difficulty was compounded by the sample being a high temperature extreme pressure oil, 2190 TEP.

The different constant relating the organic carbon standard curve to the oil standard curve was as expected because the NDIRA is operating with a lower value of gain than it was in Ref. 1.

The comparison of the synthetic seawater to the natural seawater yielded reasonable results. The natural seawater was expected to have a higher organic carbon concentration because it contains organisms (such as phytoplankton) not in the synthetic seawater. References such as 7 and 10 should be consulted for further information about seawater organism content. This difference also came about because no attempt was made to stop the processes which were occurring in seawater using methods outlined in Ref. 8. The only filtering done to the natural seawater was to remove the large particles which would not pass through the sample delivery system. This method best simulated shipboard handling techniques to obtain rapid results.

The result of 24.2 ppm organic carbon for seawater yielded by this monitoring system could be used as an

operational standard if necessary. Reference 7 reports that values obtained from natural seawater vary from location to location by orders of magnitude. Due to this uncertainty associated with natural seawater it is felt that on-site sampling as needed would yield better results especially with the reduced turn-around time now possible with the parallel system operation.

The engine room and fire room data does support Ref. 6 in that the data confirms that three distinct layers of bilge water do exist. This data shows that the carbon content of the middle layer will be less than the carbon content of the upper and sediment layer. The engine room bilge water test results do not yield much useful data because they were collected from bilge water which was located beneath a layer of oil approximately one quarter of an inch thick. The fire room bilge water test results concur with Ref. 6 in that the middle layer (which comprises the majority of bilge water) could be disposed of without being processed and still under the 15 ppm limit.

The bilge water samples were from only one ship and cannot be considered representative of all ships.

The comparison tests show that the monitoring system gave lower results than the CCl_4 method except for the two samples of low oil concentration (see Appendix D). The low oil sample concentration results were high because of the interference with the strip chart reading caused by the sliding block valve actuation solenoids as explained

previously. The largest difference in the results occurred in the samples which had concentrations that were beyond the range of the requirements listed for monitoring systems in the introduction or for the samples of 2190 TEP. No definite conclusion can be stated because of the small number of samples processed. It is to be cited that:

1. Several of the results shown in Table XII differ only by 2 ppm.
2. The system accuracy as reported by Ref. 1 is ± 1.1 ppm.
3. The oil calibration curve was linear, and
4. The NSDRL samples were randomly selected (see Appendix D).

This indicates that more samples in the range of the system should be processed.

The Monel total carbon combustion tube deteriorated because it was heated to a temperature which was slightly above the upper limit of its manufacturer's specifications. This high temperature brought about the high oxidation rate which caused the metal to flake and fall off from all surfaces.

The TC combustion tube and furnace should be developed further to reduce the heat transferred to the other system components.

The operating parameter reduction is contributed to three things. First, the operating length of the system was halved, therefore effectively reducing the system's

resistance one-half. Secondly, operating the system in parallel placed a higher pressure on the TC combustion tube inlet than was allowed while operating in the tandem configuration. Thirdly, the nichrome wires used to support the catalyst and catalyst packing in the replacement IC combustion tube did not occupy as much of the tube's cross sectional area as did the indentations used for the same purpose in the original Vycor glass tube.

X. FUTURE IMPROVEMENTS AND RECOMMENDATIONS

The improvements discussed in this section are intended to achieve a real time sample analysis, to improve the present output, or to obtain better results from the injected samples. The system at present does not appear to be operating at its highest potential. This is evidenced by it being able to maintain the temperature of the furnaces constant, to produce little or no condensate from the IC condensers, and to operate with a reduced flow rate and pressure. This is further evidenced by the NDIRAs technical manuals describing the analyzers as continuous flow analyzers.

. There are several improvements that could still be done to the sample delivery system to overcome the two problems associated with it. The first problem to be overcome is being able to obtain the TC and IC results from the same sample. Presently the system requires a completely homogeneous sample. The system presently extracts the TC sample from one part of the sample fluid stream and then extracts the IC sample at a later time from a different part of the fluid stream.

A delivery system which could alleviate this problem is shown in Figure 21. This would split the fluid stream to permit parts of the same sample to pass to the different combustion tubes. Careful attention would have to be given to use equal lengths of tubing in order to have the sample parts arrive at the same time. Consideration could also

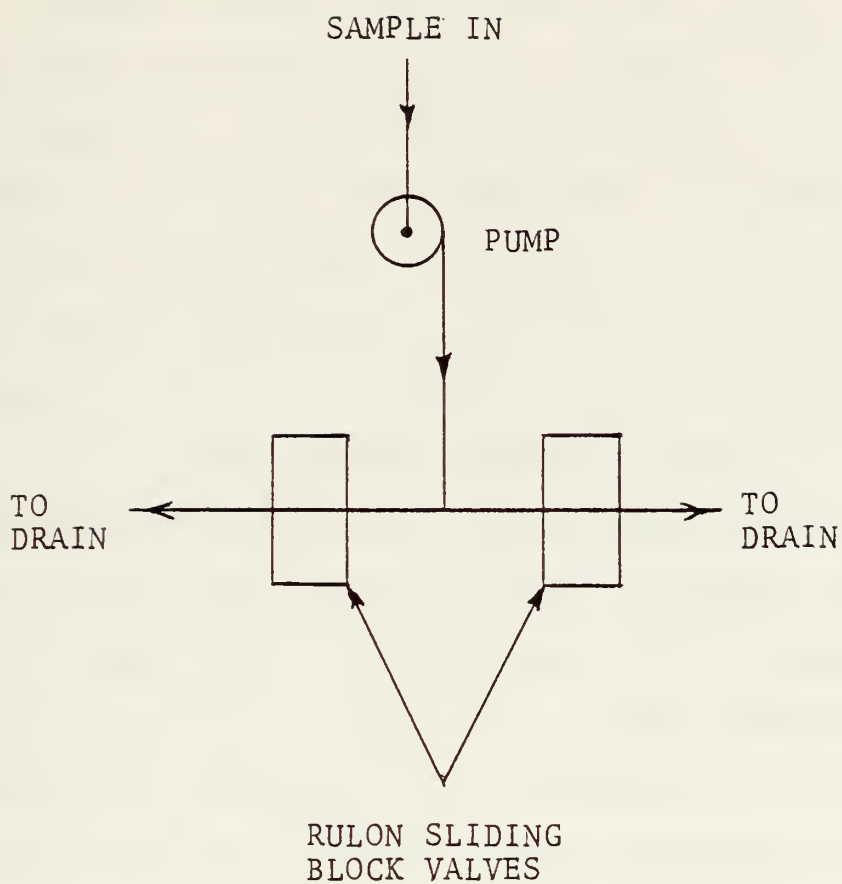


FIGURE 21. SAMPLE DELIVERY SYSTEM
IMPROVEMENT POSSIBILITY

be given to mounting the pump between the sliding block valves.

Another problem encountered which affects the sample delivery system concerned the solenoids which control the sliding block valves introducing spurious signals into the control circuits of the strip chart recorders. These spurious signals could be eliminated either by isolating the systems electrically or by using the sliding block valves to their full capability as shown in Figure 22. The sliding block valves presently used have three inlets and outlets as shown but the sliding block has four ports. The overall objective is to inject a sample into the middle outlet when the block repositions itself without interrupting the carrier gas or sample flow. This arrangement would require the solenoids to be energized or de-energized only when a sample is injected, thus eliminating the requirement to reposition the sliding block valves. The sliding block manufacturer (Ionics) should be consulted in this regard.

In order to approach a real time analysis two further refinements could be investigated. The first would decrease the time between sample injections by increasing the speed of the D. C. motor which drives the cams. This would not allow the NDIRA time to return to the baseline. The system presently depends upon peak heights to determine its output. It is possible that the sample-inject/Furnace module could supply pockets of gas to the NDIRA at a rate fast enough to produce a fairly constant output which resembles

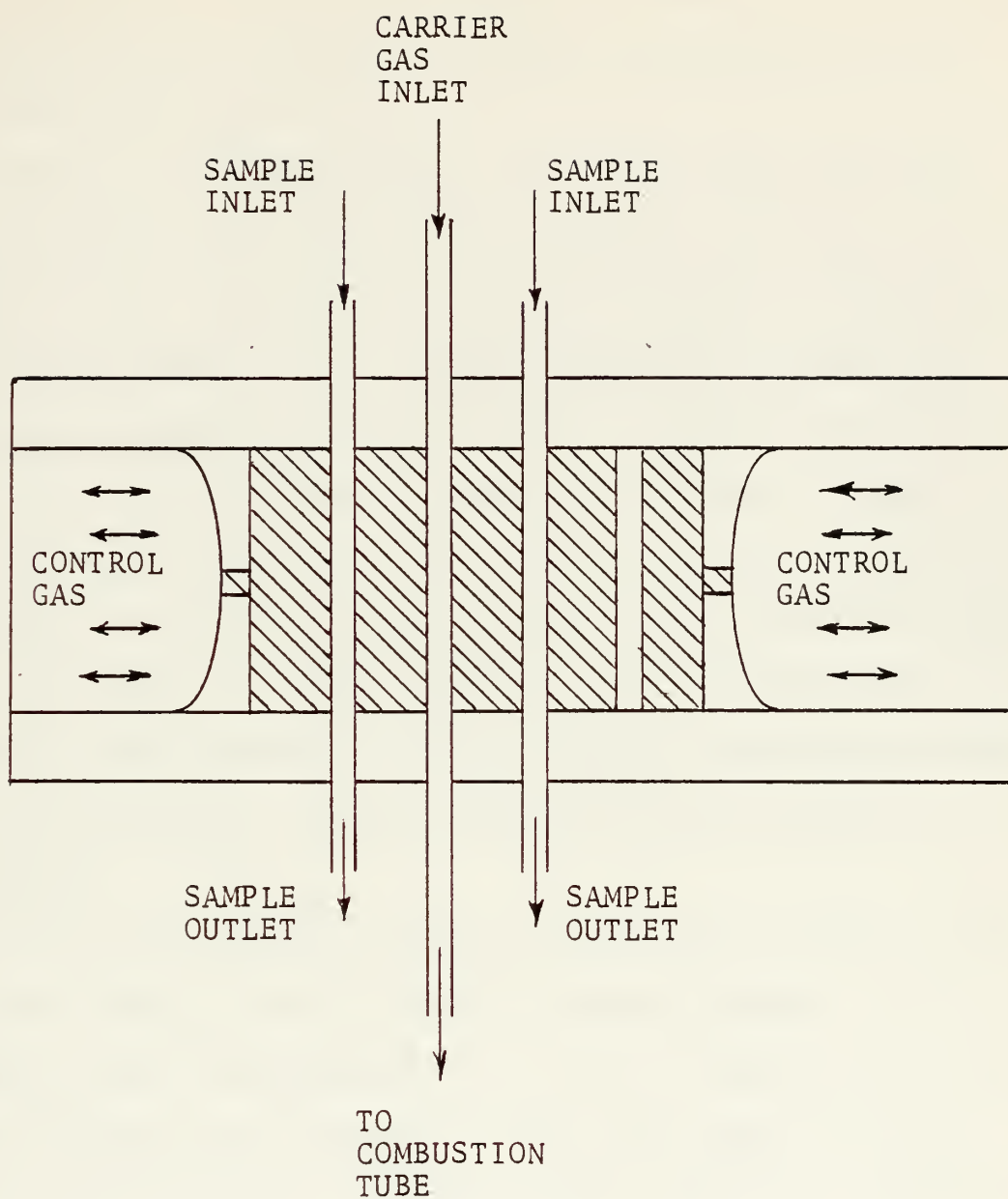


FIGURE 22. SLIDING BLOCK VALVE
IMPROVEMENT POSSIBILITY

the function $A + B \sin t$ as shown in Figure 23. The system operating now as a parallel system is a special case of this function with $A = B$.

As the system approaches a real time basis it would be necessary to investigate the transient response of the system to quick changes of samples and sample concentrations. This would require a fast acting manifold to replace the plexiglass manifold shown in Figure 3. Figure 24 shows a manifold with electrically controlled solenoid valves and the control schematic that could replace the plexiglass manifold. This system could control three different samples once the piping has been filled and the entrapped air was removed. Upon operation, three samples--the purging agent, the cleaning agent, and the sample analyzed--could be processed.

Presently the system output is an analog system. This could be replaced with an entire digital system. A micro computer with the capability to store 10 numbers could be used to provide the average of the peak heights as new peaks are processed. The peak heights could be supplied to the computer from a peak reading voltmeter.

If the pulsed system becomes operational, methods of electronic integration could be employed to determine the system output.

As the system approaches a real time basis the interplay between operating parameters is expected to cause problems. The first problem anticipated is maintaining the temperature

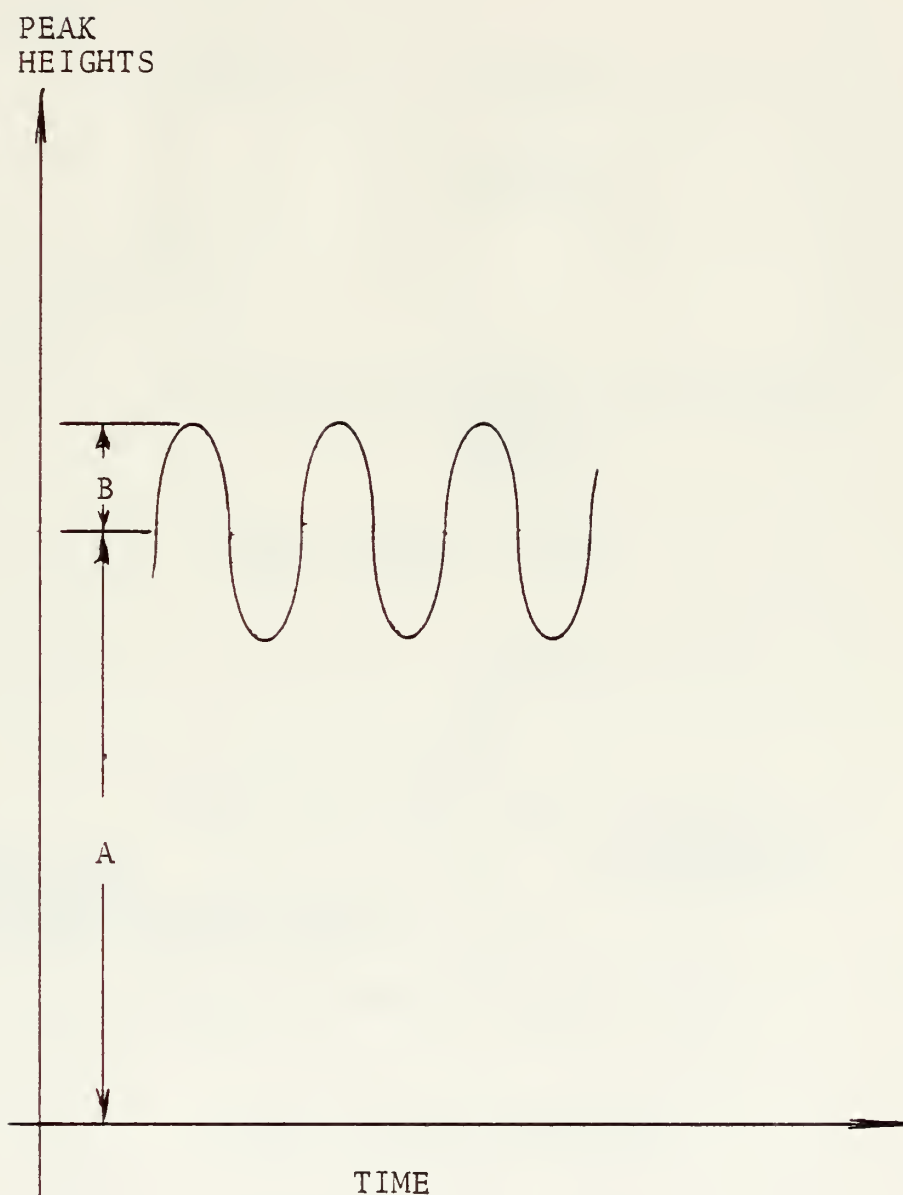
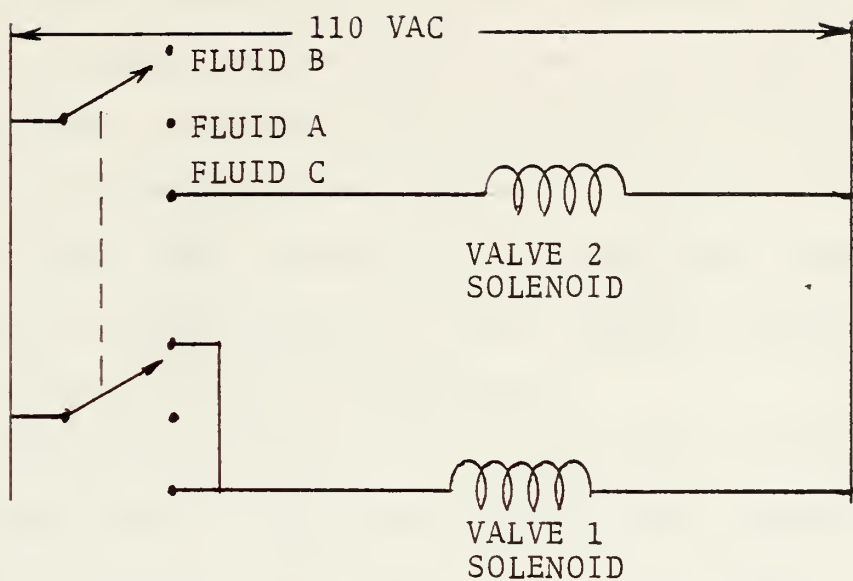
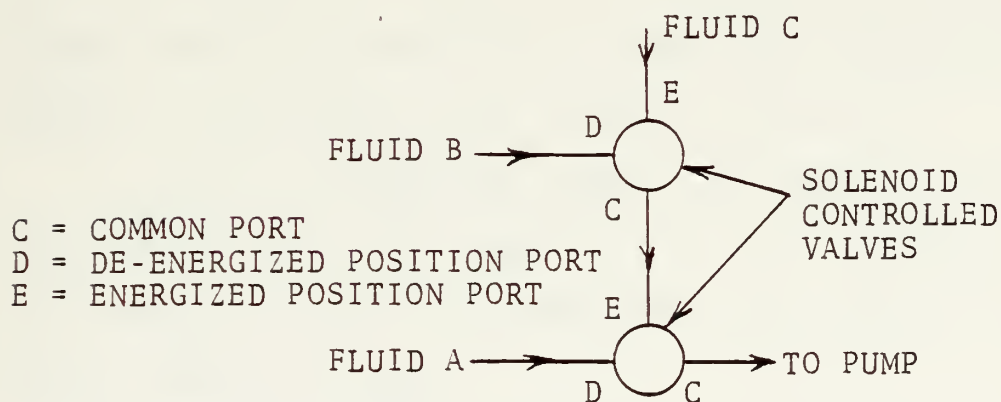


FIGURE 23. RAPID PULSE SYSTEM EXPECTED OUTPUT



POWER CONTROL CIRCUIT



FLUID CONTROL SCHEMATIC

FIGURE 24. FAST ACTING SAMPLE SUPPLY MANIFOLD

of the IC furnace. In this regard, the waste heat from the TC furnace could be used to preheat the sample before it is injected into the IC furnace. The heat transferred into the condenser by the metal connections would have to be eliminated. The most sensitive problem to be overcome would be attainment of the optimum flow rates and pressures that still meet the criteria for a monitoring system as outlined in the introduction if the digital system or the rapidly pulsed system is constructed.

The parallel system as constituted now is a large and cumbersome system. The system could be made compact by mounting the furnaces in their original horizontal position and by mounting the condensers behind the furnace in a vertical position. This would necessitate relocating the sample delivery system and orienting the sliding block valves in positions at the front of the device.

In order to reduce the number of components in the system, a single power supply and control network could be assembled to drive the Masterflex pump, the D. C. cam motor, and the B input.

The material selected to replace the ceramic TC combustion tube has to operate at a high temperature and at the same time not transfer heat to the other components of the system. This type of material will have to be a composite material or a method to remove heat from the TC condenser will have to be determined.

APPENDIX A

PARALLEL SYSTEM OPERATION AND CALIBRATION

A. OPERATION

If the system has been calibrated previously turn the high and low temperature oven to ON and increase the flow rate to about 100 cc/min. Turn the NDIRA to tune and observe the meter reading to make sure it is within the necessary limits. If not, refer to the manufacturer's technical manuals for corrective procedure. Then turn the NDIRAs to range 1. Open the sliding block activation gas cylinder and adjust the output until it reaches 35 psi. Adjust the CO₂ free air cylinder output to 10 psi.

Once the ovens reach their operating temperatures, adjust the carrier air to three psi and 150 cc/min. Process several injections of distilled water until constant peak heights are obtained and a steady baseline develops. Change the sample being processed to one which will produce an IC and TC output. Tap water is recommended. Adjust the D.C. power supply voltage until the NDIRAs have just enough time to return to the baseline before responding to the next sample. Adjust the carrier gas flow rate and pressure until the IC NDIRA output follows the TC NDIRA's output but both output peaks attain their peak heights in the same time interval.

If a constant is to be subtracted from the peak heights adjust input B until the baseline is moved the amount

corresponding to this constant. The new reference baseline should be noted on the strip chart recorder. The system is now ready for operation.

B. CALIBRATION

In order to maintain meaningful results both NDIRAs used must produce the same peak heights for the same sample. The system operating parameters are listed in Appendix B. The following steps are recommended to calibrate the system:

1. Calibrate, balance, and zero the TC NDIRA following the manufacturer's procedures.
2. Balance and zero the IC NDIRA following the manufacturer's procedures.
3. Reconnect the system components to operate as a parallel system.
4. Process several samples of distilled water to determine its average TC content.
5. Process several samples of an IC standard until a baseline is established and constant peak heights are obtained.
6. Determine the average of the TC peak heights of step 5.
7. Subtract the distilled water average TC peak heights (step 4) from the average TC peak heights (step 6).
8. Continue processing the IC standard and adjust the gain of the IC NDIRA until the average peak height

is equal to the peak height determined in step 7.

9. Adjust the D. C. power supply voltage until the NDIRAs have just enough time to return to the baseline before responding to the next sample.
10. Adjust the carrier gas flow rate and pressure until the IC NDIRA output follows the TC NDIRA output but both outputs attain their peak heights at the same time.
11. Adjust input B to the appropriate magnitude for the samples expected to be processed. If the samples are in distilled water input B would be the results of step 4. The baseline established before inserting input B should be marked because the TOC peak height is referenced from this baseline.

APPENDIX B
EQUIPMENT OPERATING PARAMETERS

1. Beckman Model 915 Sample-Inject/Furnace Module

A. Total Carbon Channel Specifications

- (1) Carrier Gas.....CO₂ free air
- (2) Flow rate.....150 cc/min
- (3) Pressure.....3 psi
- (4) Combustion Tube.....Ceramic
- (5) Catalyst.....Cobalt Oxide
- (6) Temperature.....950°C

B. Inorganic Carbon Channel Specifications

- (1) Carrier Gas.....CO₂ free air
- (2) Flow rate.....150 cc/min
- (3) Pressure.....3 psi
- (4) Combustion Tube.....Monel
- (5) Catalyst.....85% Phosphoric Acid-
Soaked Quartz chips

2. Non-dispersive Infrared Analyzer

A. Beckman Model 215B at a gain of 28

B. Beckman Model 865 at a gain of 630

3. Hewlett Packard Potentiometric 10-inch strip chart
recorders set for 0.2 in/min

A. Channel 1 -- 200 mv range

B. Channel 2 -- 200 mv range

4. Ionics Sliding Block Valves at a 35 psi switching pressure
 - A. IC channel 20 μ l sample size
 - B. TC channel 40 μ l sample size
5. Analog Module amplifier gains set at 1
6. Masterflex Tubing pump speed control set at 3

APPENDIX C

PREPARATION OF SYNTHETIC SEAWATER

To prepare nine liters of synthetic seawater:

1. Place 203.218 grams of MgCl_2 in a one-liter flask and fill to the mark with distilled water.
2. Place 73.493 grams of CaCl_2 in a 500 milliliter flask and fill to the mark with distilled water.
3. Place 1.3327 grams of SrCl_2 in a 50 milliliter flask and fill to the mark with distilled water.
4. Weigh and place in a 1500 milliliter beaker:

Substance	Grams	Substance	Grams
NaCl	215.334	NaHCO_3	1.764
Na	36.072	KBr	0.882
KCl	6.093	NaF	0.027

Add distilled water until the total weight is 1000 grams.

5. Pour the mixture of step 4 into a suitable container large enough to hold nine liters.
6. Place in the large beaker:

Substance	Volume in ml	Prepared in step
MgCl_2	479.43	1
CaCl_2	92.97	2
SrCl_2	8.1	3

Add distilled water until the total weight is 1000 grams. Pour into the large container.

7. Add 7000 grams of distilled water and stir until thoroughly dissolved.

APPENDIX D

SAMPLE AGING CONSIDERATIONS

Reference 11 outlines a laboratory method of compensating oil-water sample results to account for the concentration loss of oil for a delay time between sample preparation and sample processing. The results of this reference can only be applied to two of the samples processed during the period of this report for comparison purposes. These two samples are samples number 12 and 22 which were within the monitoring system's capability and had aged forty days.

The range of differences between the NSRDL analysis of samples and the parallel system analysis for sample numbers 12 and 22 is approximately 1.8 to 3.8 ppm and 5.5 to 8.5 ppm respectively. Using Tables a through d of Appendix A of Ref. 11, the range of corrections which could be attributed to sample aging would be 0.7 to 1 ppm for sample 12 and to 3.5 ppm for sample 22.

Applying these corrections brings the NPS and NSRDL closer together. The conclusion is then as before that more samples should be processed to compare the two systems allowing for the additional variable aging.

APPENDIX E

CALIBRATION CURVES, CALIBRATION CURVE
DATA, TEST RESULTS, AND TEST RESULT DATA

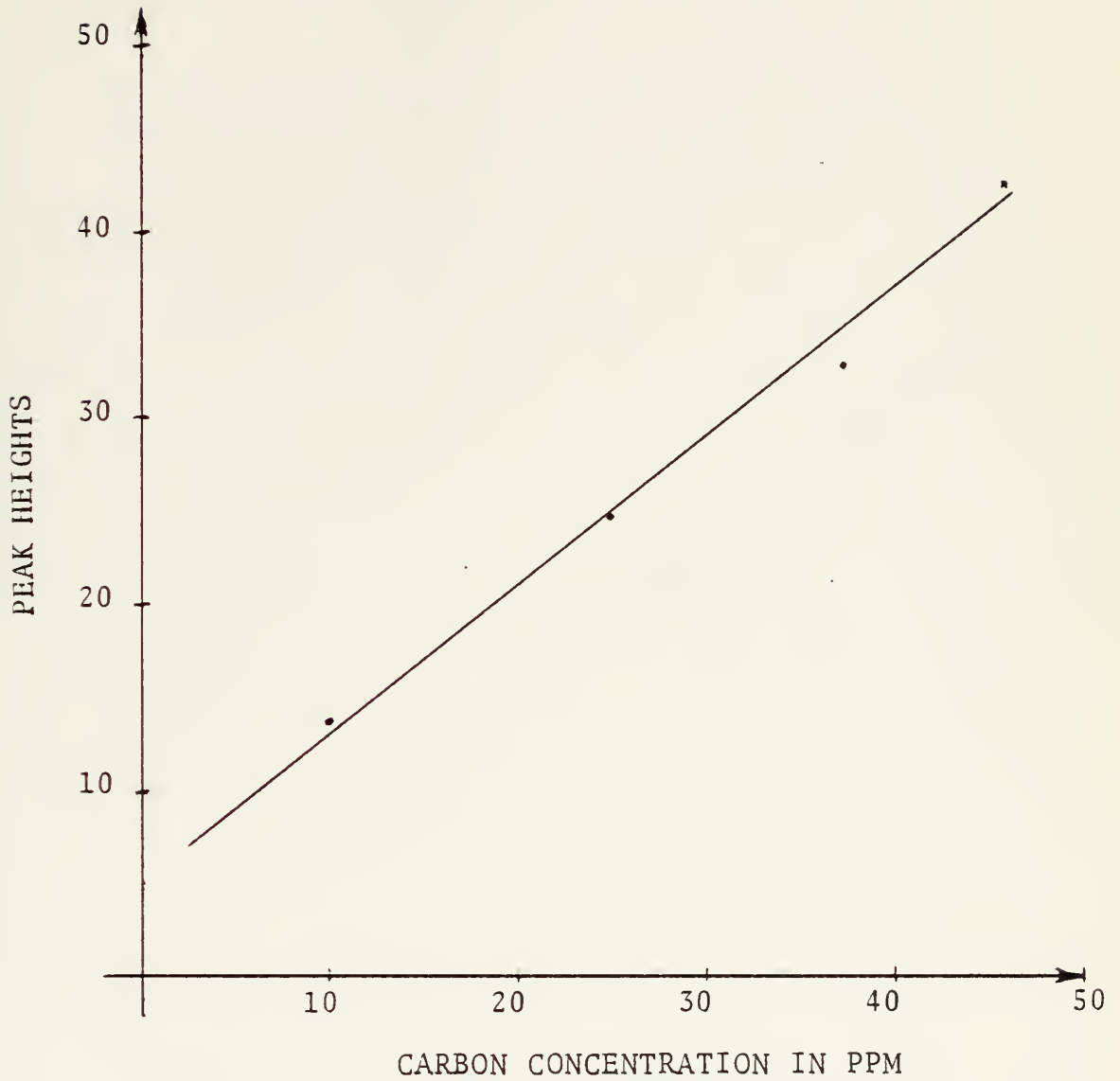


FIGURE 13. 2 FEB CALIBRATION CURVE

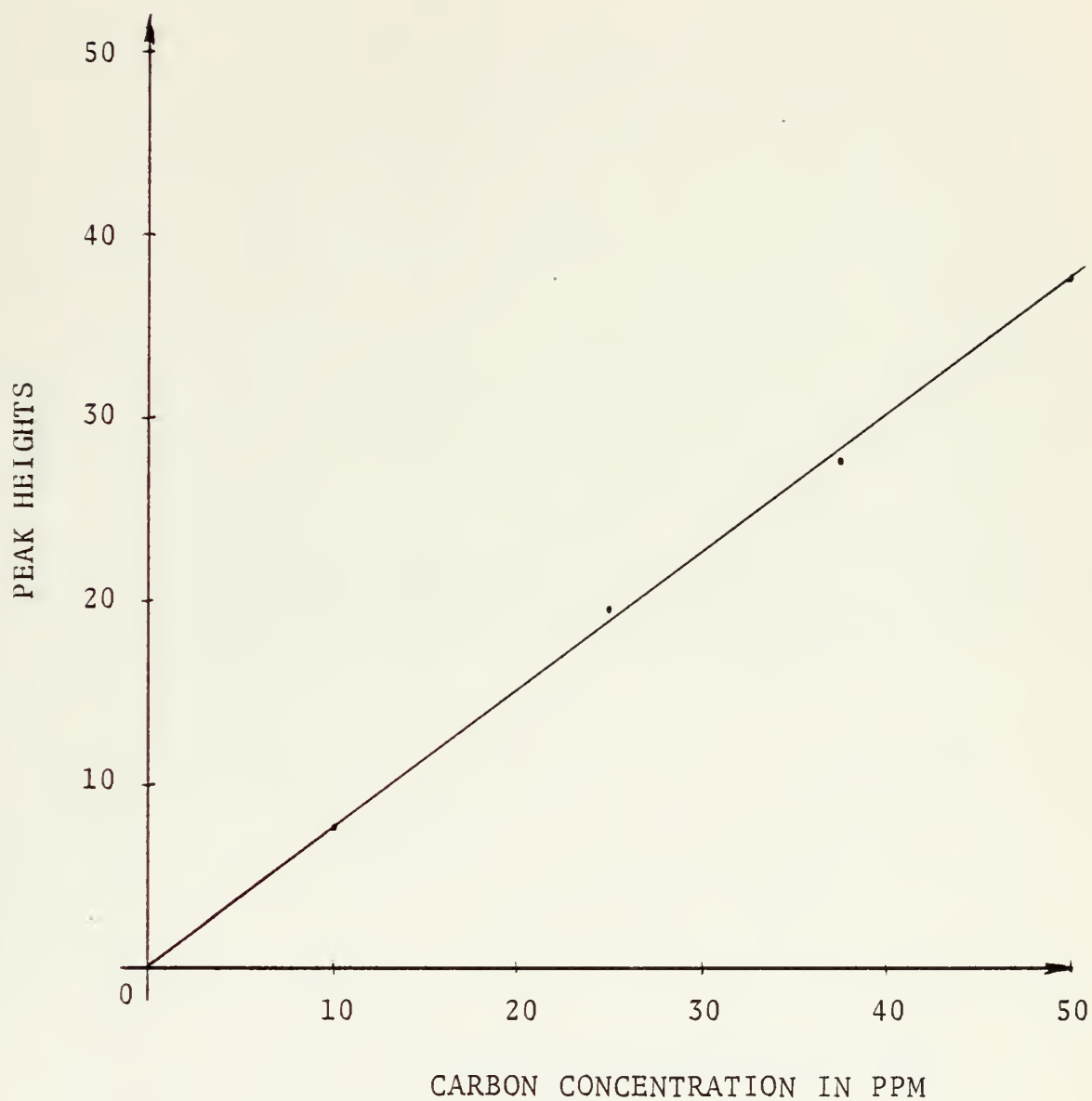


FIGURE 14. 4 APRIL CALIBRATION CURVE

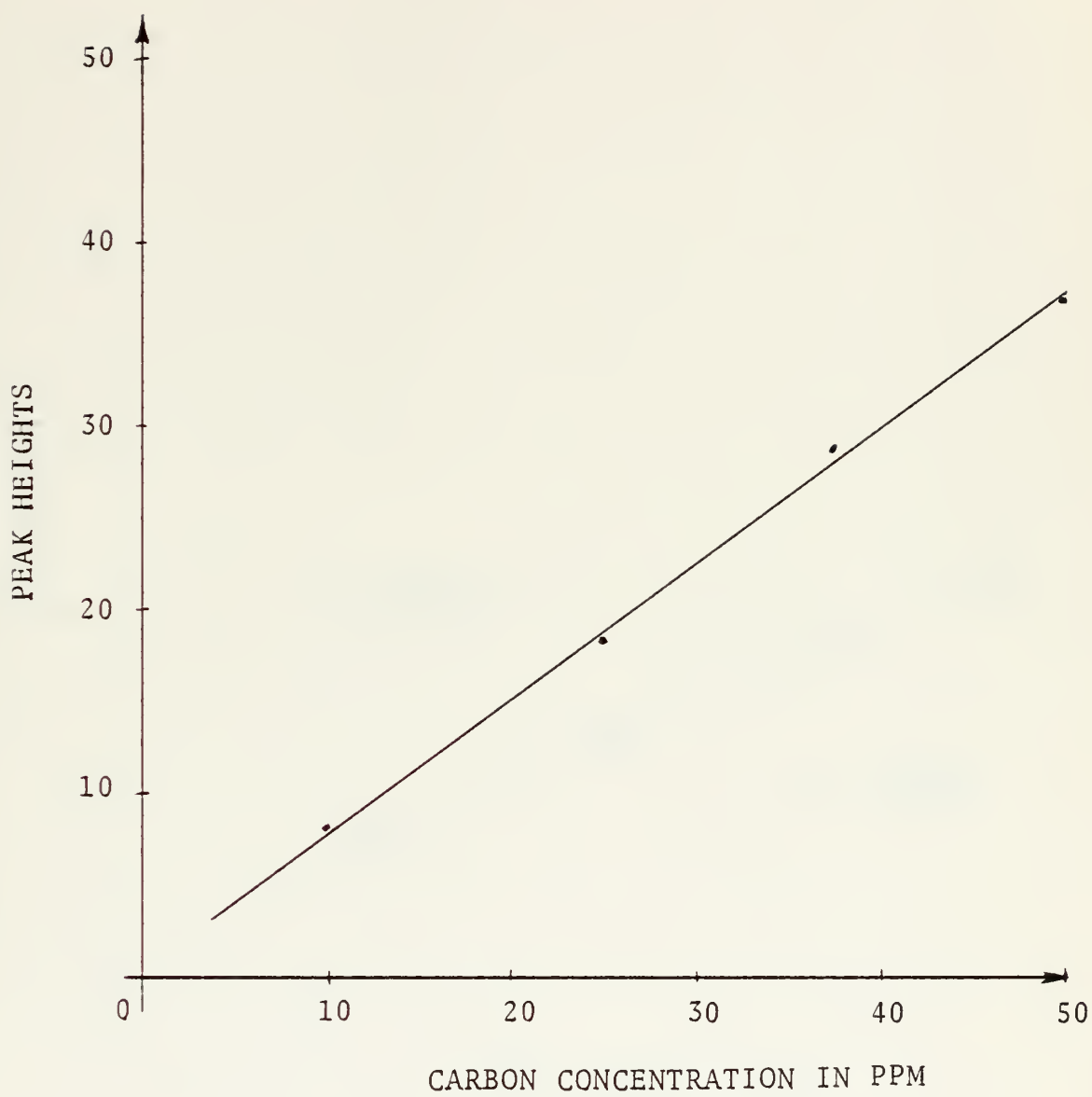


FIGURE 15. 7 APRIL CALIBRATION CURVE

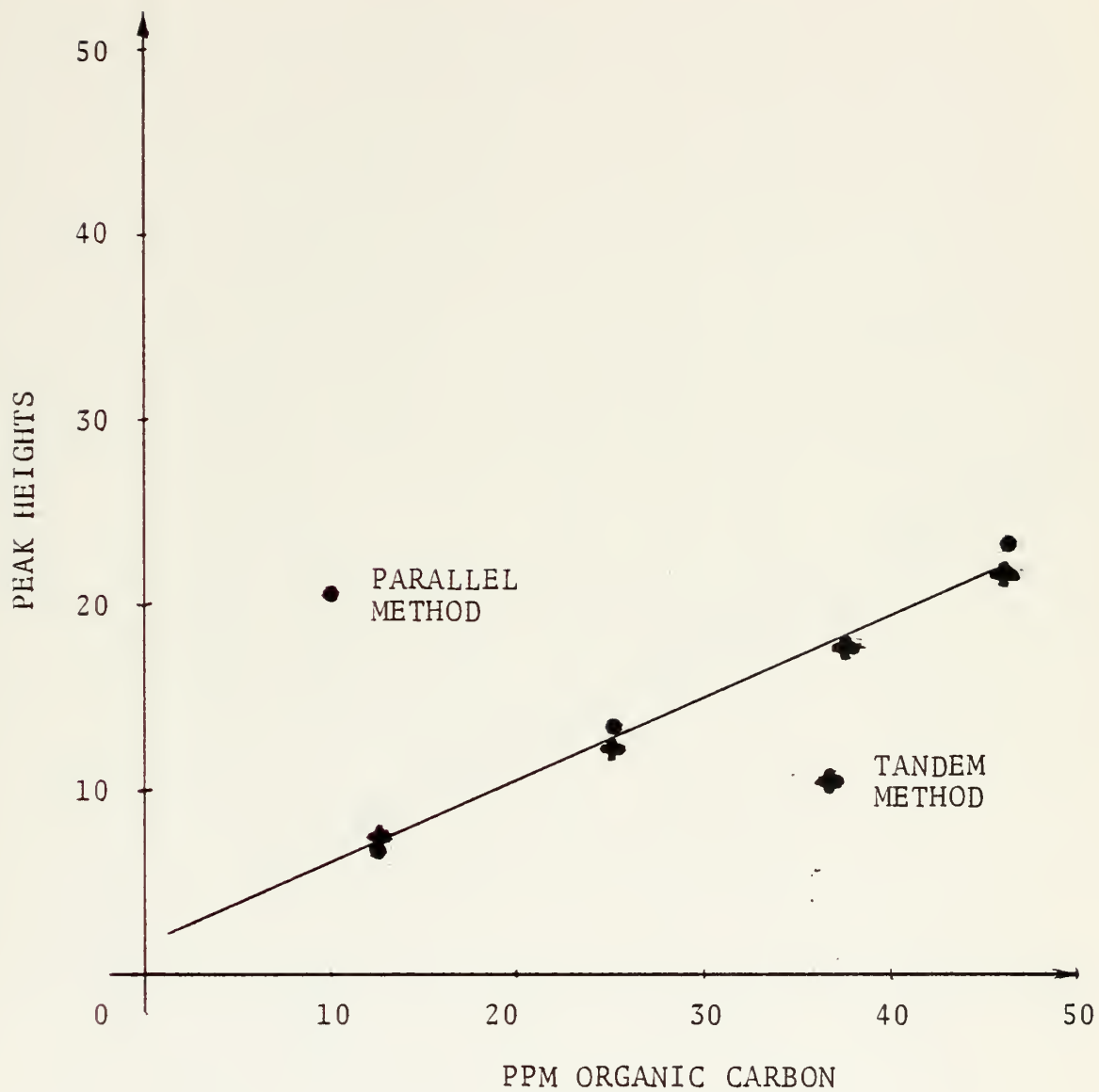


FIGURE 16. 23 APRIL CALIBRATION AND
COMPARISON CURVE

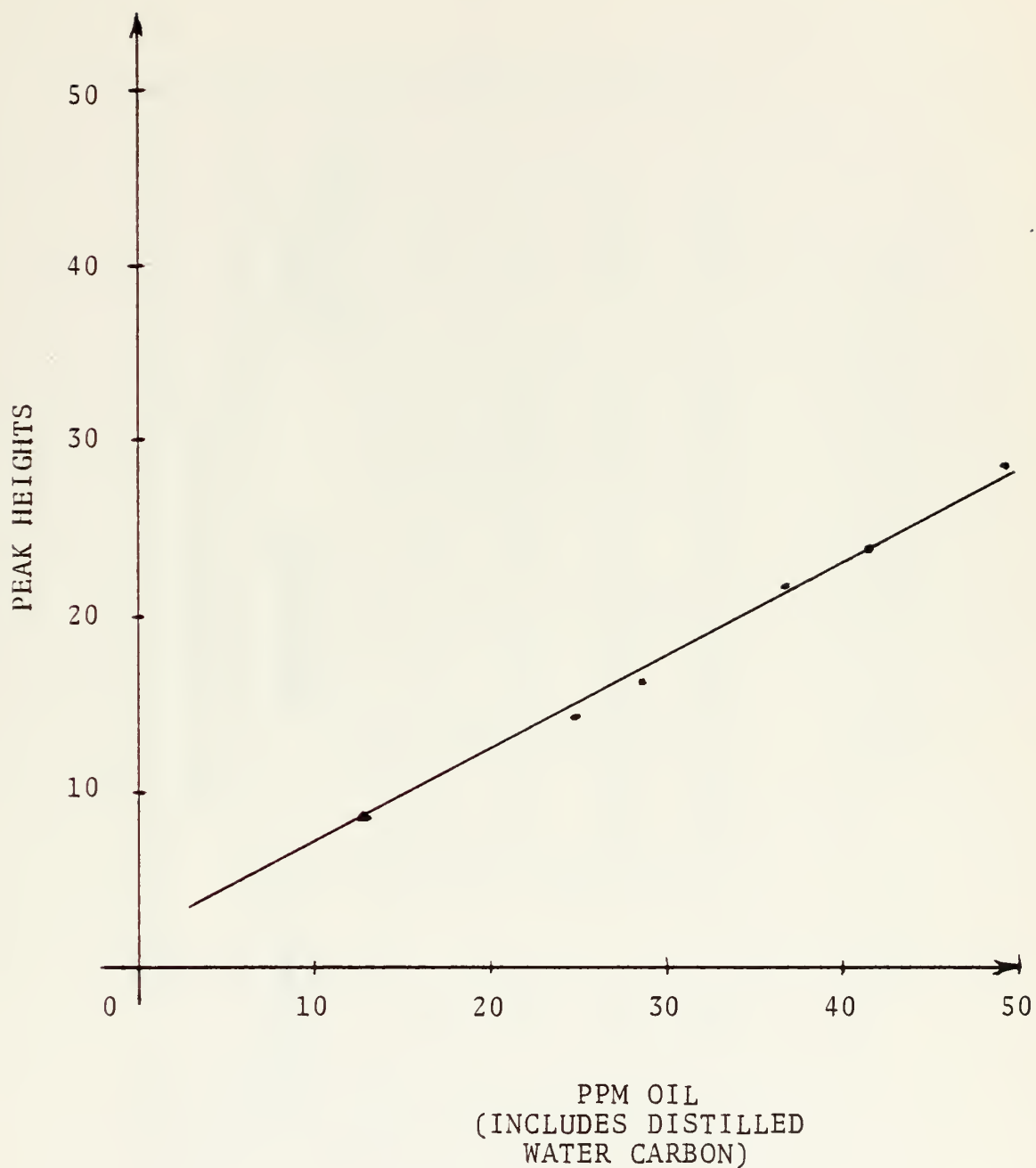


FIGURE 17. 29 APRIL 76 OIL CALIBRATION CURVE

3 FEB 76 CALIBRATION DATA					
CONCENTRATION IN PPM	COMPENSATED PEAK HEIGHTS				AVERAGE COMPENSATED PEAK HEIGHTS
50	42.3	42.3	42.5	42.2	42.3
37.5	33.2	32.8	32.3	32.4	32.7
25	24.9	24.9	24.6	24.2	24.7
10	15.4	14.3	14.0	11.2	13.73

TABLE III 3 FEB 76 CALIBRATION CURVE DATA

4 APRIL 76 CALIBRATION DATA						
CONCENTRATION IN PPM	COMPENSATED PEAK HEIGHTS				AVERAGE COMPENSATED PEAK HEIGHTS	
50	38.2	38.0	37.7	37.7	37.9	
37.5	27.8	27.8	27.7	27.8	27.8	
25	19.9	19.8	19.7	19.8	19.8	
10	8.0	8.0	8.0	7.8	7.95	

TABLE IV 4 APRIL 76 CALIBRATION CURVE DATA

7 APRIL 76 CALIBRATION DATA					
CONCENTRATION IN PPM	COMPENSATED PEAK HEIGHTS				AVERAGE COMPENSATED PEAK HEIGHTS
50	36.3	36.2	36.5	36.8	36.4
37.5	29.2	29.4	29.2	28.8	29.1
25	18.4	18.1	18.2	18.0	18.1
10	8.0	8.5	8.4	7.9	8.1

TABLE V 7 APRIL 76 CALIBRATION DATA

SAMPLE CONCEN- TRATION IN PPM	TANDEM SYSTEM TOTAL CARBON COMPENSATED PEAK HEIGHTS					
50	34.6	34.2	34.5	34.0	35.0	34.8
37.5	27.5	26.1	26.1	27.1	27.1	28.1
25	18.7	19.2	19.2	19.6	19.9	19.3
12.5	12.5	11.5	11.9	11.9	12.2	12.9
SAMPLE CONCEN- TRATION IN PPM	TANDEM SYSTEM INORGANIC CARBON COMPENSATED PEAK HEIGHTS					
50	10.2	11.8	11.3	10.6	11.8	12.1
37.5	7.6	8.0	7.9	6.3	8.8	7.8
25	5.5	5.5	5.5	5.7	5.9	5.6
12.5	3.2	3.2	3.2	3.2	3.1	3.1
SAMPLE CONCEN- TRATION IN PPM	PARALLEL SYSTEM ORGANIC CARBON COMPENSATED PEAK HEIGHTS					
50	22.5	23.4	22.6	23.0	22.3	23.8
37.5	17.3	19.6	15.8	17.7	18.4	17.9
25	13.7	13.1	12.8	14.5	13.1	13.2
12.5	8.0	5.9	7.5	7.5	8.0	4.8

TABLE VI 23 APRIL 76 COMPARISON AND
CALIBRATION CURVE DATA

SAMPLE CONCEN- TRATION IN PPM	AVERAGED COMPENSATED PEAK HEIGHTS					STANDARD DEVIATIONS		
	TC	IC	DISTILLED WATER	TANDEM SYSTEM ORGANIC CARBON	PARALLEL SYSTEM ORGANIC CARBON	TC	IC	PARALLEL SYSTEM ORGANIC CARBON
50	34.5	11.3	1.5	21.7	22.9	0.37	0.75	0.75
37.5	27.0	7.7	1.5	17.8	17.8	0.81	0.81	1.25
25	19.3	5.6	1.5	12.2	13.4	0.40	0.16	0.61
12.5	12.2	3.2	1.5	7.5	6.95	0.49	0.05	1.3

TABLE VI (CONTINUED) COMPARISON CALIBRATION CURVE DATA

OIL CONCENTRATION CALIBRATION CURVE DATA										
SAMPLE CONCENTRATION IN PPM	COMPENSATED PEAK HEIGHTS								AVERAGE PEAK HEIGHTS	
49.2	28.3	29.4	29.8	29.3	28.6	28.7	27.6	27.4	28.6	
41.6	23.6	23.6	23.6	23.7	23.5	23.3	23.8	23.8	23.6	
37.0	21.9	21.9	22.3	21.4	21.3	21.3	21.3	21.1	21.6	
28.8	16.2	16.3	16.3	16.0	16.0	16.1	16.5		16.2	
25.0	14.9	14.7	14.6	14.9	14.2	14.1	14.0	14.1	14.1	
13.0	8.7	8.7	8.7	8.8	8.8	9.0	9.0	9.0	8.8	

TABLE VII OIL CONCENTRATION CALIBRATION CURVE DATA

SYNTHETIC SEAWATER RESULTS									
DATE	NUMBER OF SAMPLES	TC AVERAGED COMPENSATED		IC AVERAGED COMPENSATED		OC AVERAGED COMPENSATED		OC IN PPM	
		PEAK HEIGHTS	STANDARD DEVIATION	PEAK HEIGHTS	STANDARD DEVIATION	PEAK HEIGHTS	STANDARD DEVIATION		
3 FEB 76	19	20.3	3.74		2.1	0.74	--	--	25.3
7 APR 76	20	25.3	0.42		6.3	1.00	--	--	24.6
26 APR 76	20	--	--		--	--	12.6	1.26	22.8

TABLE VIII SYNTHETIC SEAWATER RESULTS

SYNTHETIC SEA WATER DATA COMPENSATED PEAK HEIGHTS				
3 FEB 76		7 APRIL 76		26 APR 76
TC	IC	TC	IC	OC
27.2	1.2	25.1	6.4	12.8
30.6	2.0	25.8	6.2	12.2
19.0	1.8	25.6	4.5	11.1
27.6	2.6	25.0	5.2	12.7
16.5	3.8	25.1	6.2	12.2
21.1	2.4	25.6	4.8	11.4
27.7	3.7	25.5	6.5	10.9
25.5	1.7	25.1	6.4	11.6
19.9	1.4	25.4	6.1	10.8
22.8	2.6	25.7	6.5	11.5

TABLE IX SYNTHETIC SEA WATER DATA

SYNTHETIC SEA WATER DATA COMPENSATED PEAK HEIGHTS				
3 FEB 76		7 APRIL 76		26 APR 76
TC	IC	TC	IC	OC
27.3	2.7	25.3	6.5	14.1
22.0	2.3	25.2	4.6	13.9
20.1	1.3	24.8	6.1	15.0
24.6	2.0	25.1	6.5	11.6
25.6	1.3	25.2	6.5	13.9
23.9	2.8	25.1	7.2	12.5
24.8	2.3	24.8	6.3	14.1
20.0	2.1	26.1	7.9	12.8
27.5	2.0	24.9	8.3	13.3
		25.5	7.3	14.0

TABLE IX (CONTINUED) SYNTHETIC SEAWATER DATA

NATURAL SEAWATER RESULTS								
DATE	NUMBER OF SAMPLES	TC AVERAGED COMPENSATED		IC AVERAGED COMPENSATED		OC AVERAGED COMPENSATED		OC IN PPM
		PEAK HEIGHTS	STANDARD DEVIATION	PEAK HEIGHTS	STANDARD DEVIATION	PEAK HEIGHTS	STANDARD DEVIATION	
7 APR 76	16	26.0	0.53	6.55	1.40	--	--	26.0
4 APR 76	20	29.8	0.33	8.0	0.76	--	--	28.8
26 APR 76	20	--	--	--	--	15.3	1.79	31.8

TABLE X NATURAL SEAWATER RESULTS

NATURAL SEAWATER DATA COMPENSATED PEAK HEIGHTS				
4 APRIL 76		7 APRIL 76		26 APR 76
TC	IC	TC	IC	OC
30.0	9.4	25.5	7.7	15.8
29.8	8.7	25.4	7.6	12.4
29.9	7.2	25.1	4.6	16.2
30.2	8.5	25.7	7.2	16.3
29.2	8.2	25.7	8.1	16.0
29.6	7.9	25.9	5.8	12.7
30.0	7.0	25.7	3.8	13.2
29.3	8.3	25.7	7.0	13.7
30.2	8.8	25.8	4.3	12.9
30.4	7.1	25.7	8.1	14.2

TABLE XI NATURAL SEAWATER DATA

NATURAL SEAWATER COMPENSATED PEAK HEIGHTS				
4 APR 76		7 APR 76		26 APR 76
TC	IC	TC	IC	OC
29.9	8.1	26.3	7.6	15.6
29.7	7.6	27.4	6.9	16.1
30.0	7.9	26.5	7.5	17.8
29.7	6.2	26.5	7.3	13.0
29.4	8.6	26.5	5.1	17.9
29.4	8.0	26.7	6.2	17.9
29.8	7.5			15.5
30.0	8.1			16.9
29.8	8.9			16.3
30.3	8.7			15.9

TABLE XI (CONTINUED) NATURAL SEA WATER DATA

COMPARISON BETWEEN PARALLEL SYSTEM AND CCl_4 I.R. - SPECTROMETER METHOD				
SAMPLE NUMBER	AVERAGE PEAK HEIGHT	STANDARD DEVIATION	OIL CONCEN- TRATION IN PPM	CCl_4 METHOD OIL CONCENTRA- TION RANGE IN PPM
2	5.5	0.91	8.5	5 - 7
12	9.7	0.31	16.2	18-20
22	15.5	0.5	26.5	32-35
32	30.7	1.0	54.5	55-64
32A	24.3	0.67	42.5	52-68
22A	19.4	0.93	33.6	45-60
2A	4.7	0.53	7.0	4

TABLE XII COMPARISON BETWEEN PARALLEL
SYSTEM AND CCl_4 I.R. -
SPECTROMETER METHOD

SAMPLE LOCATION BY LAYERS	PEAK HEIGHTS									
	43.2	43.1	44.6	44.6	44.6	43.3	45.2	46.5	46.5	45.4
ER SURFACE										
ER SEDIMENT	77.5	78.6	77.0	77.5	77.5	78.1	77.8			
ER MIDDLE	17.5	18.1	16.5	17.2	17.2	16.8	18.3	17.7	17.9	18.3
FR SURFACE	82.2	81.8	87.8	84.8	84.8	84.7	84.7			
FR SEDIMENT	13.2	12.9	12.3	12.6	12.6	12.9	12.5	10.9	13.1	12.8
FR MIDDLE	8.4	8.5	8.2	8.9	8.9	7.8				

ER = ENGINE ROOM

FR = FIRE ROOM

TABLE XIII BILGE WATER TEST RESULTS

SAMPLE LOCATION BY LAYERS	AVERAGE PEAK HEIGHTS	PPM	STANDARD DEVIATION
ER SURFACE	44.7	BSC	1.32
ER SEDIMENT	77.7	BSC	0.53
ER MIDDLE	17.6	30.2	0.64
FR SURFACE	84.3	BSC	2.16
FR SEDIMENT	12.6	21.4	0.69
FR MIDDLE	8.4	14.0	0.4

BSC = BEYOND THE SCOPE OF THE CALIBRATION CURVE

TABLE XIII (CONTINUED) BILGE WATER TEST RESULTS

LIST OF REFERENCES

1. Tyler, B. D., Development of an Oil-Water Pollution Monitoring System, M. S. Thesis, Naval Postgraduate School, Monterey, California, 1975.
2. Modern Plastics Encyclopedia 1974-1975, v. 51, no. 10A, page 554, October, 1974.
3. Cole-Parmer Instrument and Equipment Co., Instruction Manual for Masterflex Tubing Pumps, 1967.
4. A. M. Castle and Company, Castle Metals Handbook, Section L.
5. Allegheny Ludlum Steel Corporation, Stainless Steel Handbook, 1956.
6. Smookler, A. L. and Hardin, J. W., Navy Shipboard Investigation of Oily Wastes, paper presented at 1975 Conference on Prevention and Control of Oil Pollution, San Francisco, California, 25-27 March 1975.
7. Anikouchine, W. A. and Sternberg, R. W., The World Ocean, Prentice-Hall, Inc., 1973.
8. American Petroleum Institute, Environmental Protection Agency, Marine Technology Society, Marine Bioassays Workshop Proceedings, 1974.
9. Beckman Instructions 015-082283, Beckman Glass Combustion Tube Charging, July 1972.
10. Wangersky, P. J., "The Organic Chemistry of Seawater," American Scientist, v. 53, p. 358, 3 September 1965.
11. Naval Ship Research and Development Center Report 4535, Determining the Concentration of Oil in Water Samples by Infrared Spectrophotometry Phase I - Sample Aging Study, by Stanley Finger, Harry Feingold, et al., Appendix A, December 1974.

INITIAL DISTRIBUTION LIST

	No. Copies
1. Defense Documentation Center Cameron Station Alexandria, Virginia 22314	2
2. Library, Code 0212 Naval Postgraduate School Monterey, California 93940	2
3. Department Chairman, Code 59 Department of Mechanical Engineering Naval Postgraduate School Monterey, Caliofrnia 93940	1
4. Assoc Professor T. M. Houlihan, Code 59 Hm Department of Mechanical Engineering Naval Postgraduate School Monterey, California 93940	1
5. LT William Ralph Gongaware 690 Ellen Road Newport News, Virginia 23605	1

Thesis

G5472 Gongaware

c.1

Improvement of an oil-
water pollution monitor-
ing system.

165610

Th
G5
c.1

Thesis

G5472 Gongaware

c.1

Improvement of an oil-
water pollution monitor-
ing system.

165610

thesG5472

Improvement of an oil-water pollution mo



3 2768 002 13091 6

DUDLEY KNOX LIBRARY